received in a period of 15 or 20 minutes. For comparison, the zinc sulfide and oxalic acid methods were also employed, but exact comparisons could not be made, as the amounts of sky exposure and the sensitivity curves differed in the methods as employed. Meller and Warga [47] studied the effects of air contaminants on the natural light of cities. Similar data were obtained by Kunerth and Miller [48] using the Rentschler meter without the aid of a graphical recorder at Ames, Iowa. Again the units are arbitrary, merely the number of impulses per second. The curves, Figures 101 and 102, show the ultraviolet in the sun and sky light and in

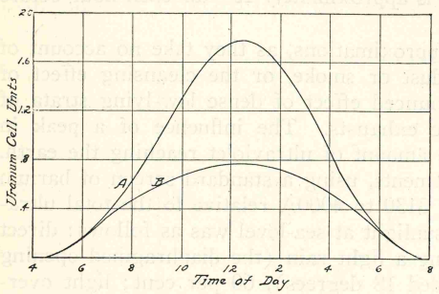


FIGURE 102.

Intensity of Ultraviolet Radiation for June 23, 1931. A. Sun and Sky. B. Sky (Kunerth and Miller, *Transactions Illuminating Engineering Society*).

the latter alone during the course of days in December and June. The energy from the north half of the sky at noon is approximately equal to one-fifth of the total from sun and sky combined. The variation of sky and sun ultraviolet with altitude of the sun and with month of the year are given in tables. The presence of snow on the ground increases the ultraviolet from sun and sky by about 20 per cent. From the data obtained by the meter exposed to sources otherwise calibrated, it appeared that each impulse of the meter was equal to about 39,000 ergs or 3000 ergs per square centimeter. These authors also presented curves for the visible region from the sun and sky and from the latter alone. The total flux on a horizontal plane throughout the year at latitude 42°N if all days are clear is 16,820,000 lumen-hours per square foot, of which 11,870,000 are received in spring and summer and 4,950,000 in autumn and winter. At noon at the winter solstice, the light from the sky is approximately 16 per cent of the total; at the summer solstice, it is 10 per cent.

At New Orleans, the average daily amount of direct solar radiation of wavelengths less than 3130A is less than 0.001 calorie per square centimeter from April to October and between 0.001 and 0.002 during the rest of the year. For the prevention of leg weakness in chickens, the amount required is about 0.00069 calorie per square centimeter daily.[49]

[47] Meller, H. B., and Warga, M. E., *Am. J. Public Health*, **23**, 217 (1933).
[48] Kunerth, W., and Miller, R. D., *Trans. Illum. Eng. Soc.*, **27**, 88 (1932).
[49] Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, **102**, 422 (1932).

Part II

Photochemical Processes

Chapter 12

Introduction to the Mechanism of Photochemical Processes

Among the earliest photochemical phenomena observed were the influence of light on the bleaching of linen, and the fading of certain natural dyes and pigments. The effect of light in developing the green color of plants, and the ability of green plants in some way to utilize the energy of the sun in converting carbon dioxide and water to carbohydrates and oxygen were recognized shortly after chemical knowledge had progressed to a stage at which the nature of combustion had become clear. A number of phosphorescent substances early attracted much attention. The photosensitivity of silver salts played an important part in the discovery of the existence of ultraviolet light. (Chapter 1.) The effect of light in accelerating the combination of hydrogen and chlorine, the decomposition of chlorine water, and the reduction of mercuric chloride solutions containing oxalic acid were the subject of a number of early papers.[1]

Grotthuss, in 1817, in studying the fading of alcoholic solutions of ferric chloride and other iron salts, concluded that only light which is absorbed can act chemically. This rather obvious statement, now frequently called the first law of photochemistry, at first attracted little attention, as interest in the energy relations of chemical processes was not yet general. The Grotthuss law was independently rediscovered by Draper in 1843 in the course of investigations on the photochemical combination of hydrogen and chlorine.[2]

The first extensive kinetic studies of a photochemical reaction were those of Bunsen and Roscoe (1855-1862) upon the hydrogen-chlorine combination. (See Chapter 18.) The choice of this reaction was unfortunate, since it is very susceptible to the influence of traces of impurities, the presence of which gives rise to a latent period between the beginning of illumination and the start of the reaction. The observation of an induction period in a reaction so apparently simple led Bunsen and Roscoe and subsequent workers to attach undue importance to induction periods as a feature peculiar to photochemical changes. They did, however, succeed in showing that in general the amount of material transformed in a photochemical change is proportional to the product of the light intensity and the time of illumination. (Bunsen-Roscoe Law.)

Subsequently, a few other reactions were studied, including the oxidation of oxalic acid,[3] the drying of oils, the decomposition of amyl nitrite,[4] the polymerization of anthracene,[5] and of vinyl halides.[6] About 1900 the Italian investigator Ciamician began with Silber a series of researches in which the substances pro-

[1] For details of the history of early photochemical work, see Plotnikow, "Allgemeine Photochemie," 2nd ed., 83-105, 1936, de Gruyter, Berlin.

[2] Draper, J., *London, Edinburgh and Dublin Phil. Mag.*, **23**, 401 (1843).

[3] Mohr, F., and Wittstein, G., *Phot. Arch.*, 430, **1864**.

[4] Tyndall, *Jahresb. Chem.*, 108, **1868**.

[5] Fritsche, J., *J. prakt. Chem.*, **101**, 337 (1866); **106**, 274 (1869).

[6] Baumann, E., *Ann. Chem.*, **163**, 317 (1872).

duced by the prolonged action of sunlight upon a wide variety of organic compounds were identified.

During the first two decades of the present century, the development of the subject of the kinetics of chemical reactions led Bodenstein, Nernst and others to attempt the interpretation of the data on the rates of photochemical reactions in terms of the law of mass action. The difference between the rates of a given reaction occurring in light and in darkness was at first attributed merely to an effect of the light in increasing the velocity constant in the simple mass law expression, no consideration being given to the possibility of a difference in mechanism in the two cases. Attempts were made, although unsuccessfully, by Wildermann [7] to treat the function of the light energy in a fashion analogous to the manner in which Faraday treated electrical energy in the study of electrolysis.

In the case of a few reactions the attempt was made to introduce the intensity of the incident light I_0 in the expressions formulated for the reaction kinetics,[8] as for example, rate $= k' I_0 [A]^m [B]^n$. Van't Hoff in 1904 introduced the assumption that the amount of substance transformed in a reaction is proportional to the amount of the light energy absorbed, rather than merely to the incident intensity, and thereby gave quantitative significance to the Grotthuss-Draper law. Attempts to determine whether or not all of the absorbed energy is effective photochemically were made, notably by Luther and Weigert [9] for the anthracene-dianthracene equilibrium, by Goldberg [10] for the photo-oxidation of quinine by chromic acid, and by Lasareff for the bleaching of dyes.[11]

During this period there were also a number of theoretical studies of photochemical reactions, some dealing with mechanism and others with thermodynamic considerations.[12] Real progress had, however, to await the contributions of the physicist. In the first place, on the practical side, the development of the quartz mercury-vapor arc (Chapter 6) greatly stimulated the study of reactions following the absorption of ultraviolet rays, studies of the wave-length dependence of the yield soon appearing in great number. On the theoretical side, the development of the quantum theory (Chapters 1 and 2) for the first time permitted a beginning to be made in the approach to a satisfactory comprehension of the mechanism by which radiant energy may be absorbed by molecules. Before considering these mechanisms (Chapter 13) it is necessary to discuss the general physical laws of absorption.

The loss in radiant energy of a beam of light which occurs during its passage through a cell containing a liquid or a gas is ascribed to three processes; (a), reflection at the surfaces, (b) scattering by any dust particles in the gas or by colloidal particles in the liquid and (c) absorption by the molecules of the gas or liquid. The last of these is the only one of importance photochemically. In homogeneous pure liquids, scattering may usually be neglected.

Lambert showed that the absorption of approximately monochromatic light varies exponentially with the thickness of the absorbing layer, or $I_x = I_0 e^{-\beta x}$ in which I_0 and I_x denote the incident and transmitted light intensities, x is the

[7] Wildermann, M., *Z. physik. Chem.*, **42**, 257 (1902); Smits, A., and Aten, A., *Z. Elektrochem.*, **16**, 264 (1910); *Chem. Abs.*, **4**, 1842 (1910).

[8] Bunsen and Roscoe in the hydrogen chlorine reaction and Gros, O., *Z. physik. Chem.*, **37**, 157 (1901).

[9] Luther, R., and Weigert, F., *Z. physik. Chem.*, **53**, 385 (1905).

[10] Goldberg, E., *Z. wiss. Phot.*, **4**, 61 (1906).

[11] Lasareff, P., *Ann. Phys.*, **24**, 661 (1907); **37**, 812 (1912).

[12] Tian, A., *Compt. rend.*, **156**, 1601 (1913); Henri, V., *Soc. Franc. d. Phys.*, **12**, 2 (1911); Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 1597 (1912); **156**, 889 (1913); **160**, 519 (1915).

thickness of the absorbing layer and β is a number characteristic of the absorbing substance and called its absorption coefficient. Its value varies with the wave-length in a manner characteristic of the substance.

In 1852, Beer found that in the case of solutions, β is proportional to the concentration, c, of the absorbing component. β may therefore be replaced by αc, α being the absorption coefficient of the absorbing component of the solution. (In cases in which the solute is modified by or reacts with the solvent, Beer's law does not hold.) About this time, Stokes made extensive studies of the phenomenon of fluorescence, which consists in the emission of light of certain wave-lengths by a substance during the time in which it is being irradiated by light of (usually) other wave-lengths. He found that the wave-lengths of the emitted rays are greater than those of the exciting rays. (Stokes's Law.)

The Einstein Photochemical Equivalence Law

Of the utmost importance to the subsequent development of photochemistry was the derivation by Einstein [13] of the photoequivalent law which states that each absorbed quantum should cause one light-absorbing molecule to react. The derivation of this law, obtained from Planck's radiation law by thermodynamic reasoning, lies beyond the scope of this book. It implies that the number of molecules which have absorbed monochromatic radiant energy may be obtained by dividing the total absorbed energy in ergs (measured physically) by the energy $h\nu$ of a single quantum of light of the frequency employed. To facilitate the evaluation of the quanta of various frequencies commonly employed in photochemistry, Bodenstein and Wagner [14] proposed to employ the term einstein for the energy of N (the Avogadro number, 6.06×10^{23}) light quanta, this being the energy absorbed when each molecule of a gram-molecular weight of a substance absorbs a quantum of radiant energy. They suggested that the intensity of absorbed light be expressed in einsteins absorbed per liter per second.

The idea that the rate of a photochemical reaction may be determined by the number of light quanta absorbed per second had been expressed by Stark as early as 1908 [15] preceding the derivation of the photochemical equivalent law by Einstein. Stark believed the primary effect of the light absorbed to be a loosening of the valence electrons, rendering the molecule chemically active. He also distinguished between the primary process of the absorption of light by a molecule and the subsequent secondary processes initiated by the light-changed molecule.

The value of the einstein is commonly expressed in kilocalories for photochemical work. It may be calculated by multiplying the frequency by Planck's constant h (6.54×10^{-27} erg-seconds) and by N (6.06×10^{23}) and dividing the result by 4.182×10^{10} to convert ergs into kilocalories. If the wave-length in Ångström units is first converted into the wave-number by the aid of the graph at the right of Figure 103 it may easily be converted into kilocalories by multiplication by the factor 0.00285. Even this calculation may be avoided by the use of the curve (A *vs.* kcal.) in the same figure.

An appreciation of the magnitude of the einstein at various wave-lengths is of value in enabling one to predict the possibility of effecting a reaction of known activation energy by the use of a given wave-length known to be absorbed by the reacting system.

[13] Einstein, A., *Ann. Physik*, **37**, 832 (1912); **38**, 881 (1913).

[14] Bodenstein, M., and Wagner, C., *Z. physik. Chem.*, **3B**, 456 (1929).

[15] Stark, J., *Physik. Z.*, **9**, 898 (1908).

It is convenient to remember that 10,000A, where the wave-number is also 10,000, corresponds to 28.47 kcal. Then at 5000A the wave-number will be twice as great since it is the reciprocal of the wave-length which is half of 10,000A; the heat value will, therefore, be twice 28.47 or 56.94 kcal. The wave-length, 4000A corresponds to 71 kcal., 3000A to 94.6 kcal. and 2000A to 142.1 kcal. In the x-ray region the values become enormous, but in the far infrared they decrease to such small values as 0.285 kcal. at 100μ.

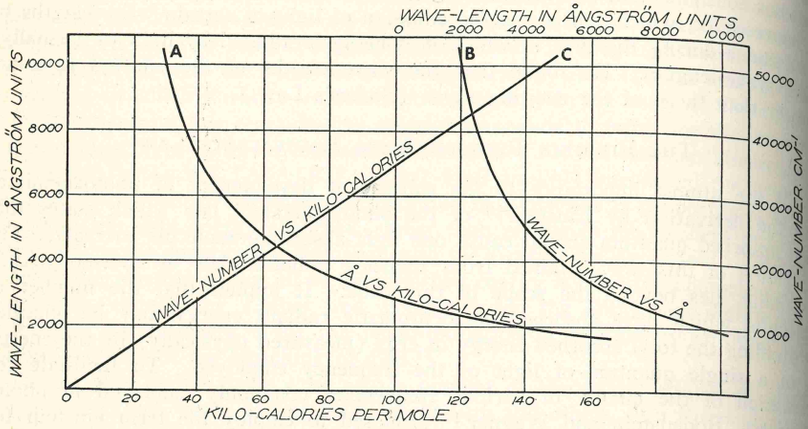


FIGURE 103. Graphs for Conversion of Wave-lengths and Wave-numbers into Kilo-calories per Mole and for Conversion of Ångstrom Units into Wave-numbers.

Most photochemical reactions follow upon a process of absorption in which the configuration of the valence electrons has been in some manner altered, and it will be shown in Chapter 13 that visible or ultraviolet radiation is usually required to produce such an electron shift. In the infrared region, the absorbed energy is usually insufficient to produce such effects and instead serves only to alter the rotational motion of the molecule as a whole or the vibrational motion of its component atomic nuclei with respect to each other.[16] There is no fundamental distinction between the reactions due to visible or ultraviolet light and it is not feasible to discuss their effects separately. In order adequately to discuss the effects produced by ultraviolet light it will frequently be necessary to disregard the limitation set by the title of this book and to discuss many reactions due to the absorption of visible light.

Little is known of reactions which may be induced in the regions between the Schumann and the usual x-ray regions. Palmer[17] has noted that radiations from a hydrogen discharge tube passing through a fluorite window into air cause the formation on the outside of the window of a film with metallic luster (soluble in alcohol) which probably is calcium oxyfluoride, and upon the latter a white powder insoluble in water and soluble in dilute hydrochloric acid. Both deposits impede the passage of rays of wave-lengths between 1250 and 1500A.

Reactions Produced by X-Rays. These reactions have received far less study than those produced in the visible and ultraviolet regions. The direct photo-

[16] Mecke, R., *Trans. Faraday Soc.*, **27**, 359 (1931).
[17] Palmer, F., Jr., *J. Chem. Physics*, **2**, 296 (1934).

chemical absorption of the radiation plays a role subordinate to the effects of photoelectrons. The enormous energies of the x-rays make it possible for one quantum on ionizing a molecule to endow the resulting photoelectron with great amounts of kinetic energy.[18] Subsequent effects bear some resemblance to the reactions produced by the bombardment of a substrate with a stream of high-velocity electrons.[19]

According to Risse,[20] and Fricke and Brownscombe[21] pure, oxygen-free water is not decomposed by x-rays. Comparatively few inorganic reactions have been studied. Noteworthy among these are the hydrogen-chlorine combination,[22] the decomposition of hydrogen peroxide and of potassium persulfate,[23] and certain changes induced in ferrous sulfate,[24] chromic acid,[25] iodine[26] and on photographic plates.[27] Among organic compounds, chloroform and iodoform have been the most extensively studied; hydrogen halides are liberated along with other less investigated products.[28]

General reviews of the chemical effects of x-rays, which in the main are much less extensive than those produced by ultraviolet rays, have been given by Glocker,[29] Günther,[30] Clark and Pickett,[31] and by Fricke.[32] Fricke states that a pecularity of x-ray action is that it frequently involves the production of molecules with unusually high energy states, such as water molecules with at least 91 kcal. per gram molecule.

The Infrared Region. With the possible exception of certain explosions, which may be influenced by infrared radiations,[33] no established case of a chemical reaction brought about by these radiations could be cited by Daniels in 1928.[34] Many attempts were, however, made to find such reactions because of the stimulus of the radiation theory of the origin of the activation energy for chemical reactions, now nearly universally abandoned. This theory which was first suggested by Trautz,[35] and elaborated by Lewis,[36] Perrin,[37] and others,[38] held that the necessary activation energy calculated from the temperature coefficient by the Arrhenius equation, is obtained by absorption by the

[18] Dauvillier, A., *Compt. rend.*, **171**, 627 (1920).
[19] For a further discussion of this topic, see Simons, L., *Brit. J. Radiology* (*Roentgen Soc.*, Sect. 23), 124 (1927), or the article of Faila, G., in Duggar, "The Biological Effects of Radiations." New York, McGraw-Hill, **1936**.
[20] Risse, O., *Z. physik. Chem.*, **140**, 133 (1929).
[21] Fricke, H., and Brownscombe, E. R., *Strahlentherapie*, **26**, 319 (1929); **24**, 749, 757 (1927); Fricke, H., and Washburn, M., *Phys. Rev.*, **40**, 1033 (1932); Fricke, H., and Brownscombe, E. R., *Ibid.*, **44**, 240 (1933); Fricke, H., *J. Chem. Phys.*, **2**, 349 (1934).
[22] Leblanc, M., and Volmer, M., *Z. Elektrochem.*, **20**, 494 (1914); Götzky, S., and Günther, P., *Z. physik. Chem.*, **26B**, 373 (1934).
[23] Glockler, R., and Risse, O., *Z. Physik*, **48**, 845 (1928).
[24] Shishacow, W., *Phil. Mag.*, **14**, 198 (1932); Fricke, H., *loc. cit.*
[25] Fricke, H., and Washburn, M., *loc. cit.*
[26] Bordier, H., *Compt. rend.*, **163**, 291 (1916).
[27] Eggert, J., and Noddack, W., *Ber. deutsche physik. Ges.*, 23 (**1924**); Günther, P., and Tittel, H., *Z. Elektrochem.*, **39**, 647 (1933); de Moncetz, A. *Compt. rend.*, **184**, 284 (1927); Villard, P., *Compt. rend.*, **184**, 131, 309, 352 (1927); **186**, 1669 (1928).
[28] Glocker, R., *Z. tech. Physik.*, **7**, 571 (1926); *Z. Physik*, **43**, 827 (1927); **46**, 764 (1928); Günther, P., *Angew. Chem.*, **46**, 627 (1933); Hill, D., *J. Am. Chem. Soc.*, **54**, 32 (1932).
[29] Glocker, R., *Z. tech. Physik*, **9**, 201 (1928).
[30] Günther, P., *Angew. Chem.*, **41**, 1357 (1928); *Ergebnisse tech. Röntgenkunde*, **4**, 100 (1934).
[31] Clark, G. L., and Pickett, L. W., *J. Am. Chem. Soc.*, **52**, 465 (1930); Clark, G. L., and Coe, W. S., *J. Chem. Phys.*, **5**, 97 (1937).
[32] Fricke, H., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 55 (1935).
[33] David, W. T., *Proc. Roy. Soc.*, **108A**, 617 (1925).
[34] Daniels, F., *Chem. Rev.*, **5**, 56 (1928).
[35] Trautz, M., *Z. wiss. Phot.*, **4**, 160 (1906); *Z. anorg. Chem.*, **102**, 81 (1917).
[36] Lewis, W. C. M., *J. Chem. Soc.*, **113**, 471 (1918); *Phil. Mag.*, **39**, 26 (1920).
[37] Perrin, J., *Ann. Phys.*, **11**, 5 (1919); *Trans. Faraday Soc.*, **17**, 546 (1922); *Compt. rend.*, **187**, 913 (1928).
[38] Baly, E. C. C., *Phil. Mag.*, **40**, 1, 15 (1920); *Rec. trav. chim.*, **41**, 516 (1922).

reacting molecules of the black-body radiation from the surrounding molecules or from the walls of the vessel. Were this the case it would obviously be possible to calculate from the activation energy, the frequencies at which the radiation should be absorbed, by equating the energy in ergs to Nhv.

The hypothesis was soon opposed on theoretical grounds largely concerned with calculations of the inability of activation by this method to supply energy fast enough to account for the observed rates of reactions.[39] Modifications and elaborations were repeatedly proposed to meet these objections.[40] Experimentally, it was found that many substances failed to exhibit absorption bands in the regions corresponding to the wave-lengths calculated from the theory. In the case of nitrogen pentoxide, the energy of activation, 24.7 kcal., corresponds to a wave-length of 1.16 μ, but this radiation fails to produce any decomposition since it is not absorbed.[41] It was also found that longer wave-lengths were also ineffective in accelerating this reaction.[42] Similar negative results have also been reported for the racemization of pinene.[43]

A few workers have, however, reported instances of reactions which appeared to favor the theory.[44] Dhar and Bhattacharya[45] claimed some forty reactions which occur in darkness may be slightly accelerated by radiation of wave-length 7304A. They interpret the wave-length corresponding to the activation energy (derived from temperature coefficients) as a threshold wave-length for photochemical action. Rao and Dhar[46] have extended this point of view and attempted to support it by extrapolating the yields of four photochemical reactions observed at various wave-lengths to determine the long-wave limit at which the yield is zero. This threshold was believed to coincide with that calculated from the activation energies.

The Applicability of the Einstein Law

Not until the radiation theory had risen and begun to fall did any large number of workers turn to an experimental study of the validity of the Einstein equivalent law. A few, however, notably Bodenstein and Warburg, were early interested in correlating the absorbed energy with the amounts of materials entering into reaction. Very shortly after the appearance of the Einstein theory, Winther[47] and Bodenstein[48] assembled the available data from the literature and made rough calculations to test the applicability of the Einstein law. The quantum yield may be defined as the number of molecules which react for each quantum of light absorbed. The data available in the literature were inadequate for an accurate estimation of the quantum yields, since in most cases the absorbed energy values could be estimated only from the absorption coefficients of the substances studied and from the distances of the reaction mixtures from the sources. These crude approximations nevertheless served to indicate that the quantum yields may range from values as low as 0.05 in the case of the oxidation of quinine to 10^6 in the combination of hydrogen and chlorine. In but two of twenty reactions for which these admittedly rough calculations could be made was the quantum yield found

[39] Langmuir, I., *J. Am. Chem. Soc.*, **42**, 2190 (1920); Lindemann, F. A., *Phil. Mag.*, 40, 671 (1920); Tolman, R. C., *J. Am. Chem. Soc.*, **42**, 2506 (1920); **43**, 269 (1921); **47**, 1542 (1925).

[40] Lewis, W. C., and McKeown, A., *J. Am. Chem. Soc.*, **43**, 1288 (1921); Garner, W. E., *Phil. Mag.*, **49**, 463 (1925); Lewis, G. N., and Smith, D. F., *J. Am. Chem. Soc.*, **47**, 1508 (1925); Rice, J., *Trans. Faraday Soc.*, **21**, 494 (1926); Ornstein, *Z. physik. Chem.*, **120**, 98 (1926); Roy, S. C., *Trans. Faraday Soc.*, **21**, 512 (1926).

[41] Daniels, F., and Johnston, E. H., *J. Am. Chem. Soc.*, **43**, 72 (1921).

[42] Kassel, L. S., *J. Am. Chem. Soc.*, **51**, 54 (1929); Rice, F. O., Urey, H. C., and Washburne, R. N., *Ibid.*, **50**, 2402 (1928).

[43] Ure, W., and Tolman, R. C., *J. Am. Chem. Soc.*, **51**, 974 (1929).

[44] Audubert, R., *Compt. rend.*, **184**, 881 (1927); Rideal, E. K., and Hawkins, J. A., *J. Chem. Soc.*, **117**, 1288 (1920).

[45] Dhar, N. R., and Bhattacharya, A. K., *Trans. Faraday Soc.*, **26**, 1 (1930); *J. Indian Chem. Soc.*, **6**, 143, 451 (1929).

[46] Rao, G. G., and Dhar, N. R., *J. Phys. Chem.*, **36**, 646 (1932).

[47] Winther, C., *Z. wiss. Phot.*, **11**, 92 (1913).

[48] Bodenstein, M., *Z. physik. Chem.*, **85**, 329 (1913). The most recent tabulation of the quantum yields (120 reactions) is due to Daniels, F., *J. Phys. Chem.*, **42**, 713 (1938). He has also summarized advances in technique, *Ibid.*, **42**, 701 (1938).

to approach unity, the value required by the Einstein law. Bodenstein suggested that the first step of the reaction, the absorption of light, should be called the primary process and that it is to this only that the Einstein law properly pertains. He believed that the primary process is characterized by the fact that each molecule absorbs one quantum (or a small number of quanta) and is altered thereby, this process being uninfluenced by temperature[48a] or the presence of foreign substances. The subsequent secondary processes, which follow the law of mass action, may be quite complex and may cause the quantum yield of the overall reaction to vary from unity.

Bodenstein's conception of the nature of the change provoked in a primary process was that it consisted (in analogy with the photoelectric effect) in the expulsion of electrons from the absorbing molecules leading to the formation of ions, which then took part in the secondary processes. This is now known to be the case in few if any photochemical reactions. Bodenstein himself later discarded this for other conceptions of the nature of the primary process. He also suggested the term "acceptor" for the substance which reacts in a secondary process with the primary product formed by the absorption of light by a molecule. If the attempt were made to test the validity of the Einstein law for the primary process, it would be necessary to find an acceptor that would react with the primary product at a rate equivalent to that of the primary reaction. To him it appeared that the problem of experimentally testing the Einstein law resolved itself into finding suitable acceptors.

The term "acceptor" has never been widely adopted by photochemists, and attempts to prove directly the Einstein law for the primary process by searching for a suitable "acceptor" for a given absorbing molecule have given way to attempts to understand the mechanism of the processes involved in given reactions, whatever their quantum yields may be. A few studies were, however, made from this standpoint. Noddack[49] investigated the photochemical reactions between bromine and cyclohexane, and between chlorine and trichlorobromomethane and found both to follow the photoequivalence law. On the other hand, Pusch[50] stated that hydrogen is an unsuitable acceptor for light-altered bromine, but that hexahydrobenzene is a suitable one.

Among the most thorough quantitative investigations of the applicability of the Einstein law and of quantum yields were those of Warburg (which had been started even prior to the publication of the Einstein law) on the relation of energy absorbed to photochemical change. Important phases of this work dealt with the decomposition of hydrogen iodide,[51] hydrogen bromide,[52] the maleic-fumaric acid transformation,[53] the hydrogen-chlorine combination,[54] the ozone decomposition,[55] the decomposition of nitrates,[56] and of ammonia.[57] Although the details of this work will be discussed in other chapters, it may be noted here that the quantum yields found showed the same type of extreme variation that had been suggested by the rough calculations of Bodenstein, being two for the first two reactions,

[48a] This has subsequently required modification.

[49] Noddack, W., *Z. Elektrochem.*, **27**, 359 (1921); *J. Chem. Soc.*, **120** (2), 568 (1921).

[50] Pusch, L., *Z. Elektrochem.*, **24**, 336 (1918).

[51] Warburg, E., *Sitzb. Preuss. Akad.*, 300 (1918).

[52] Warburg, E., *Ibid.*, 314 (1916).

[53] Warburg, E., *Ibid.*, 360 (1919).

[54] Warburg, E., *Z. Elektrochem.*, **27**, 133 (1921).

[55] Warburg, E., *Sitzb. Preuss. Akad.*, 644 (1913); 872 (1914).

[56] Warburg, E., *Ibid.*, 1228 (1918).

[57] Warburg, E., *Ibid.*, 746 (1911); 216 (1912).

0.032 to 0.104 for the third, extremely high for the fourth, from 0.28 to 1.7 (dependent upon the presence of other gases) for the fifth, 0.024 to 0.25 for the sixth, and 0.25 for the last.

It is important to note the manner in which experiments made with three separate wave-lengths of approximately monochromatic light in the hydrogen iodide decomposition and with two wave-lengths in the case of that of hydrogen bromide afforded a strong confirmation of the theory. Since the magnitude of the quantum increases as the wave-length decreases, it is evident that for the same total amount of energy absorbed at different wave-lengths, the number of quanta absorbed decreases as the wave-length decreases. Therefore, the yield of a given process should be less when the same total energy is employed at a shorter than at a longer wave-length. In the hydrogen iodide decomposition, Warburg found that the ratio of moles decomposed to the calories absorbed (multiplied by 10^5) decreased from 2.08 at 2820A to 1.85 at 2530A and 1.447 at 2070A. The expected values calculated upon the basis of the Einstein law were 1.003, 0.89 and 0.73, respectively. These were in each case very close to half of the observed values. Therefore, in each case, the quantum yield was two. The results in the hydrogen bromide decomposition were very similar.

Warburg was also able to suggest a reasonable explanation of the quantum yield of two by assuming the primary process of absorption by the hydrogen iodide or bromide to consist in a dissociation of these molecules into atoms. A relatively simple sequence of secondary reactions, supported on thermodynamic grounds by Nernst, accounted for the observed quantum yield of two. In this way, granting the correctness of the assumed mechanism of the primary process, the observed quantum yield, despite the fact that it was not unity, could be regarded as a confirmation of the theory. The opinion gradually gained ground that when all factors were taken into account, it would be possible to devise mechanisms for the primary processes and secondary reactions for those photochemical reactions in which extreme values of the quantum yields at first sight appeared less favorable to the theory.

In summarizing his work, Warburg stated[58] that the law has been proved to apply when the quantum absorbed is greater than the energy of dissociation, although in certain cases collisions of the products of dissociation with molecules of foreign gases may lead to a dissipation of their energy so that the law is apparently not followed. He also recognized at this time that in the case of reactions effected by the absorption of quanta smaller than the heat of dissociation, the mechanism of the primary process may involve the formation of excited rather than dissociated molecules. (This type of mechanism will be considered in more detail subsequently.) In this case, under certain conditions, complicating processes may lead to a dissipation of a portion of the energy of some excited molecules so that the quantum yield may be reduced.

Perhaps the present position with regard to the Einstein law has been most clearly stated by Taylor[59] who avoids the idea of equivalence implied by earlier statements of the law by giving it in the form of this Second Law of Photochemistry:

"The absorption of light is a quantum process involving one quantum per absorbing molecule or atom. The photochemical yield is determined by the thermal reactions of the system produced by the light absorption." Henri and

[58] Warburg, E., *Naturwiss.*, **47**, 1058 (1924).
[59] Taylor, H. S., *J. Phys. Chem.*, **32**, 516 (1928).

Wurmser[60] recognized the importance of the nature of the primary process in determining the mechanism of a photochemical reaction and discussed the manner (see Chapter 14) in which fluorescence and absorption spectrum studies may be employed in determining the nature of the primary process.

Despite general acceptance of the Einstein law, the possibility has been suggested that in certain cases one quantum of incident energy may activate more than one molecule of the absorbing substance. Basu[61] suggested, possibly as an outcome of Raman spectrum interpretations (Chapter 13), that the incident quantum uses part of its energy in activating the molecule it strikes, and that the remainder is scattered and may activate another molecule.

Investigations of quantum yields have been and are still being carried out extensively because they provide data for testing proposed mechanisms for the reactions studied. Quantum yields are determined for various incident wave-lengths of radiation for each new photochemical reaction investigated. The influence upon the yields of many factors, including temperature, variations in the intensity of light, the effects of changes in pressure in gaseous reactions and of concentration in solutions, the effects of different solvents, catalysts and inhibitors, are being actively studied. The more detailed discussion of these topics is given in connection with the individual reactions considered in subsequent chapters.

Chain Reactions

Allusion has been made to the fact that in certain reactions high quantum yields have been observed. Thus in the hydrogen-chlorine combination, it was stated that the quantum yield was of the order of a million. To explain this, Nernst[62] proposed on thermodynamic grounds the possibility of the following cycle of reactions:

$$Cl_2 + h\nu \longrightarrow Cl + Cl$$
$$Cl + H_2 \longrightarrow HCl + H$$
$$H + Cl_2 \longrightarrow HCl + Cl, \text{ etc.}$$

The last two of these reactions evolve heat and can occur spontaneously and be repeated until the hydrogen and chlorine are consumed. Other reactions are conceivable, but are limited in extent. If two chlorine atoms could combine to form a chlorine molecule, they might be expected to dissociate again on absorption of another quantum of radiation. There is, however, an even more cogent reason why neither this process nor the combination of two hydrogen atoms to form molecules can occur to any considerable extent. The combination of two chlorine atoms is exothermic to the extent of 58.5 kcals. For the production of a stable molecule by a collision of two atoms it would be necessary for the energy of recombination to be removed in some manner or the atoms would move apart again. If, however, two atoms of chlorine (or of hydrogen) should chance to collide at the same time with a molecule of an inert gas or with the wall of the reaction vessel, the excess of energy might be imparted to the inert gas molecule or to the wall so that a stable molecule of chlorine (or of hydrogen) might be produced. The inability of atoms to combine to form molecules by two-body collisions thus provides one of the reasons which make it possible for the reactions written above to be so often repeated and thereby make the quantum yield so enormous. In the language of physical chemistry, the chains are said to be long.

[60] Henri, V., and Wurmser, R., *J. phys. Radium*, **8**, 289 (1927).
[61] Basu, K. P., *J. Phys. Chem.*, **33**, 1200 (1929).
[62] Nernst, W., *Sitzb. Berlin Akad. Wiss*, 65 (1911).

Although Nernst set up the reaction chain just discussed, he did not at that time suggest all of the details; many others have contributed to the building up of our present concept of chain reactions. Nernst calculated that a similar cycle would be impossible in the case of the combination of hydrogen and bromine, because the reaction $Br + H_2 \rightarrow HBr + H$ is endothermic. Actually, a mixture of hydrogen and bromine is not light sensitive at ordinary temperatures, although a chain reaction occurs at higher temperatures. A further discussion of the more detailed reasoning in regard to these reactions and also the hydrogen iodide decomposition will be given in the chapter on reactions in the gas phase. (Chapter 17.)

Many chain reactions are subject to inhibition by certain substances, which when present in traces, break the chains and lower the yields. A general discussion of the methods of determining the mechanisms of chain reactions has been given by Noyes.[63]

In interpreting the kinetics of chain reactions, three processes require consideration, (a) the chain starting process, (b) the chain terminating process and (c) the chain continuing process.[64]

The Nature of the Primary Process. During recent years an increasing amount of attention has been devoted to an exact determination of the nature of the primary processes of light absorption and the molecular changes affected thereby. Although the book by Kistiakowsky on Photochemical Processes (1928) was predominantly concerned with the kinetics of a number of complete reactions, an indication of the recent shift in emphasis is to be found in the fact that the "Foundations of Photochemistry" by Bonhoeffer and Harteck (1933) devotes 182 pages to the primary process, 39 to secondary reactions and only 59 to the kinetics of overall reactions. At present, efforts are being made to increase our knowledge of the secondary reactions.

Besides the Warburg theory of dissociation as the primary process, others have been proposed. Recent studies indicate, however, that the production of atoms or free radicals either by direct dissociation following the absorption of a quantum or by predissociation (a process described in Chapter 14) is the most commonly encountered primary process.

The early views were rather indefinite. Stark[65] thought the primary effect to be a loosening of valence electrons, rendering the molecules chemically active ("intramolecular photoelectric effect"). Baly and Rice[66] considered ordinary molecules as condensed systems which are non-reactive until opened up, and discussed the relation of absorption bands and fluorescence phenomena to this loosening process. An important paper historically was one in which Stern and Volmer,[67] on the basis of the then current interpretation of band spectra, took issue with the dissociation mechanism proposed by Warburg for the reactions of the hydrogen halides. These authors, influenced by the Bohr theory of the excitation of atoms, explained the primary process of light absorption by molecules in terms of an analogous elevation of the energy level of the molecule by the energy of the absorbed quantum. In this way they made somewhat more precise what is implied in the activation of molecules, a term which had been used earlier by Luther. They discussed particularly the possible ways in which excited molecules might

[63] Noyes, W. A., Jr., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 32 (1935); see also Semenov, N., *Acta Physicochim. U.R.S.S.*, **3**, 245 (1935).
[64] Rollefson, G. K., *J. Phys. Chem.*, **42**, 773 (1938).
[65] Stark, J., "Prinzipien der Atomdynamik," Leipzig, S. Hirzel, II, 207 (1911).
[66] Baly, E. C. C., and Rice, F. O., *J. Chem. Soc.*, **101**, 1475 (1912).
[67] Stern, O., and Volmer, M., *Z. wiss. Phot.*, **19**, 275 (1920).

dispose of their energy of excitation. In the first place the energy might be lost by re-emission (fluorescence). A second possibility is the loss of the energy of excitation by inelastic collisions with other molecules, involving conversion of energy of excitation into heat energy. The third and most important possibility is that the excited molecules on colliding with other molecules might utilize this excess energy as energy of activation in bringing about chemical reactions. Thus an activated hydrogen iodide molecule (denoted by *) on colliding with a normal molecule might cause a reaction in which a molecule of hydrogen and one of iodine are produced.

$$HI + h\nu \longrightarrow HI^*$$
$$HI^* + HI \longrightarrow H_2 + I_2$$

In this way it would be possible to explain the quantum yield of two which had been determined experimentally by Warburg.

At the time it was put forward, this view had much to recommend it. Data were being contributed by physicists on the fate of excited atoms and the manner in which the loss of their energy by fluorescence could be quenched or lessened by the presence of inert gas molecules which by collisions could remove the energy. An extension of these considerations to photochemical reactions offered an attractive opportunity for explaining the decreases in quantum yields of gas reactions often observed to occur in the presence of increasing concentrations of foreign non-absorbing gases. Furthermore, at this time relatively little was known of the behavior of atoms or free radicals and their postulation as intermediates by Warburg appeared unnecessarily artificial. Warburg indeed gave as the criterion for the occurrence of dissociation in the primary process the stipulation that the quantum energy of the absorbed radiation must be larger than the heat of dissociation of the molecules, and recognized that the absorption of lesser quanta could lead only to the production of excited molecules. For these reasons, attention during the early 1920's was predominantly devoted to the activated molecule theory of the primary process. Noddack[68] explained the lowering of the yield in the reaction between chlorine and trichlorobromomethane in carbon tetrachloride which accompanies increasing dilution by the solvent on the basis of this theory. The more frequent collisions of the activated molecules with indifferent carbon tetrachloride molecules deactivated them so that the photochemical reaction had less chance of occurring. It was also pointed out by many that if an activated molecule did not collide with a molecule with which it might react within its life period (10^{-8}–10^{-9} second)[69] it would lose some of its energy by fluorescence; if, on the other hand, it collided with an indifferent molecule it could lose its energy in the collision. In a gas at normal pressures the loss of energy by fluorescence would not be expected to be important, this effect becoming pronounced only when the time interval between collisions of the excited molecules with the reactant molecules becomes comparable with the mean life of the excited state.

Attempts were made to extend the theory of activated molecules to account for chain reactions, the assumption being made that such an excited molecule enters into reaction with a normal molecule and produces another excited molecule as one of the products in a manner analogous to that in which atoms functioned in the chain theory of Nernst. It need only be said here that such energy chains have been shown to involve certain difficulties and that, in the main, there is rarely any necessity for assuming their occurrence in explaining photochemical

[68] Noddack, W., *Z. Elektrochem.*, **27**, 359 (1921).
[69] Cf. Mukerji, B. K., and Dhar, N. R., *Z. Elektrochem.*, **31**, 283 (1925).

processes. Elaborate attempts were also made to picture the change involved in activating molecules in terms of the orbits in which the valence electrons move.[70] Such attempts have been rendered unnecessary by developments of the theory of valence and of molecular energy states.

Brief mention may be made at this point of an early theory of Weigert[71] which assumed that at least two molecules of gaseous halogens participate in the absorption process, an electron being believed to be displaced from one to the other. The resulting molecular complex acted as a nucleus at which subsequent reactions proceeded. This theory has not survived, although a vestige remains in the modern treatment of the photochemical processes occurring in alkali-halide crystals.

By 1924, Bowen,[72] in comparing the mechanisms (dissociation versus excited molecule) of the primary process involved in the photochemical reactions by which the hydrogen halides are formed showed that the dissociation theory gives a quantitative explanation of all the experimental facts if due consideration is given to the heats of reaction and if it is assumed that a large evolution of heat favors a spontaneous reaction and that an endothermic secondary reaction does not proceed. He pointed out that a clarification of the then conflicting points of view in regard to the nature of the primary process awaited a physical interpretation of the data of the band absorption spectra of gases. The most marked feature of the development during recent years has been the application of the theory of band spectra to the interpretation of the primary processes of photochemical reactions. For this reason the next chapter digresses to give a brief introduction to the theory of the origin of band spectra, after which it becomes possible in Chapter 14 to discuss the contributions which spectroscopy is able to make to an understanding of the nature of the primary process in photochemical reactions occurring in the gas phase.

[70] Waldbauer, L., and Patton, I. J., *J. Phys. Chem.*, **31**, 1433 (1927).

[71] Weigert, F., *Ann. Physik*, **24**, 243 (1907); *Z. Elektrochem.*, **28**, 456 (1922); Weigert, F., and Kellermann, K., *Z. physik. Chem.*, **107**, 1 (1923); Weigert, F., *Ibid.*, **102**, 416 (1922); **106**, 407 (1923). See, for objections, Kornfeld, G., *Z. physik.*, **108**, 118 (1924).

[72] Bowen, E. J., *J. Chem. Soc.*, **125**, 1233 (1924); *Trans. Faraday Soc.*, **21**, 543 (1925).

Chapter 13

Molecular Spectra and Their Relation to Photochemistry

Early workers on the absorption or emission spectroscopy of molecules used spectroscopes of low resolving power and observed spectra characterized by more or less regularly recurring flutings or bands. These apparently continuous bands gave rise to the term "band spectra," really a misnomer since instruments of higher resolving power have long since revealed the fact that in many cases, the "bands" in the spectra of gaseous molecules are really composed of great numbers of finely spaced lines.

Molecular spectra have been very actively investigated within the last two decades. The literature dealing with them is of vast proportions and is couched in a somewhat unfamiliar notation, unfortunately necessary because of the complexity of the interrelations between the forms of motion characterizing molecular energy states, the transitions between which give rise to the many lines. In the study of the emission spectra of molecules much effort has been required merely to identify the molecule or molecular fragment giving rise to a given spectrum or arrangement of lines and bands under the experimental conditions of excitation. In many instances it has been demonstrated that the spectrum must be attributed to the presence of molecules of a type unfamiliar to a chemist (BO, He_2, BaH, etc.).

Early investigations were limited to the accurate measurements of the wavelengths of the many lines observed in the emission or absorption spectra of various substances produced under definite experimental conditions. Later phases of the work were concerned with the identification of the molecules responsible for these spectra, and, following this, with the classification of the lines into bands, of the bands into groups of bands, and of these groups into larger series. Next came the representation of these observed facts by mathematical expressions. Only in the past thirty years has it been possible to make physical interpretations of the relationships thus demonstrated.

The study of molecular spectra has provided the chemist with a tool which has yielded data valuable in fields remote from that of photochemistry. The spectra provide information as to the structures, sizes and shapes of molecules, have led to the discovery of the isotopes of several elements and have furnished values for heats of dissociation, bond strengths, heat contents, entropies, specific heats, free energies, equilibrium constants and heats of activation in many cases more readily and more accurately than are secured by the older methods of thermochemistry.[1] Progress in the application of the methods of wave mechanics to the interpretation of band spectra has been so rapid as to have led Kemble[2] to

[1] Giauque, W. F., and Wiebe, R., *J. Am. Chem. Soc.*, **50**, 101, 2193 (1928); **52**, 4808, 4816 (1930); **53**, 507 (1931); Godnev, I. N., *Ibid.*, **58**, 180 (1936); Kassel, L. S., *Phys. Rev.* **43**, 364 (1933); *J. Am. Chem. Soc.*, **55**, 1351 (1933); *J. Chem. Physics*, **1**, 576 (1933); Zeise, H., *Z. Elektrochem.*, **39**, 758 (1933); Franck, J., *Ibid.*, **36**, 581 (1930); Bryant, W., *Ind. Eng. Chem.*, **25**, 820 (1933); Rodebush, W., *Chem. Rev.*, **9**, 319 (1931); Kassel, L. S., *Chem. Rev.*, **18**, 277 (1936); Witmer, E., *J. Am. Chem. Soc.*, **56**, 2229 (1934).

[2] Kemble, E. C., *J. Frank. Inst.*, **206**, 27 (1928).

express the hope that "in a few years we may understand the fundamental principles of molecule formation as definitely as we now understand the principles of dynamo design."

The complexities of spectra and the extensive mathematical equipment required for their interpretation make this a field for specialists. Fortunately, a detailed knowledge of this field is not essential to an understanding of much of the work in photochemistry. The discussion in this chapter is intended only to furnish the chemist not versed in spectroscopy with enough of the present viewpoint regarding molecular spectra to permit him to comprehend the manner in which the character of the spectrum within a given wave-length region shows whether the absorption has produced excited molecules or has led to a dissociation of the molecule into atoms or free radicals. The character of the molecular spectrum thus gives a clue to the nature of the primary process of absorption. For the most part, only the spectra of diatomic molecules will be considered, since these have been more completely interpreted than have the vastly more complicated spectra of polyatomic molecules.

Representative of the band spectra of diatomic molecules is that of phosphorus nitride, a portion of which is reproduced in Figure 104. Each of the dark regions which fades out gradually from a sharp edge is known as a band. Some molecules produce spectra in which the fading from the edge of the bands to more and more widely separated and weaker lines extends toward the shorter wave-lengths. In the spectra of others the opposite is true. The bands are accordingly said to be degraded toward the violet or toward the red.

The edges of the bands recur in a somewhat regular sequence and so form a band group. Furthermore, over wider spectral ranges, the various groups of bands may also follow in sequence to form a system of bands. The complete emission spectrum of a substance may under certain circumstances consist of several band systems. Cyanogen, for example, has one system between 4000 and 5000A and another in the red. Different portions of the complete spectrum may be revealed by the use of different methods of excitation. The complete spectrum of a diatomic molecule composed of unlike atoms may extend from the far infrared to far in the ultraviolet.

Deslandres,[3] a pioneer in the empirical study of molecular spectra, demonstrated relations between the wave-numbers of the lines of a band and also between those of the heads of the bands of a group. As in the case of atomic spectra, progress in the interpretation of such relationships came only with the appplication of the quantum theory. The wave-numbers of the individual lines depend upon the differences between energy states of the molecule. In discussing the possible energy levels of a molecule there must be considered certain molecular and intramolecular motions which were not encountered in the discussion of the energy levels of atoms. The molecule may rotate as a whole about its center of gravity and the two atomic nuclei may vibrate with respect to each other along the line joining their centers. Each of these types of motion is quantized, only discrete rotational and vibrational energy levels being possible. In addition, as in atomic spectra, transitions between electronic energy levels must be considered.

Even before the advent of the Bohr theory of the quantization of the electronic states of atoms, Bjerrum[4] suggested that transitions between various rotational

[3] Deslandres, H., *Compt. rend.*, **103**, 375 (1886); **104**, 972 (1888); **134**, 747 (1902); **138**, 317 (1904); *Ann. Chim. Phys.*, **15**, 5 (1888); *J. de phys.*, **10**, 276 (1891).

[4] Bjerrum, N., *Nernst Festschrift*, 90 (1912); cited in Baly, E. C. C., "Spectroscopy," Vol. 3, London, Longmans Green, 1927.

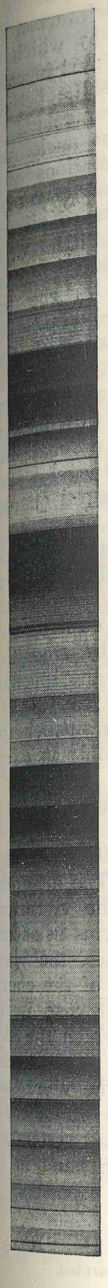


FIGURE 104. Band Spectrum of a PN Molecule (From Herzberg, "Atomic Spectra and Atomic Structure," New York, Prentice-Hall, 1937).

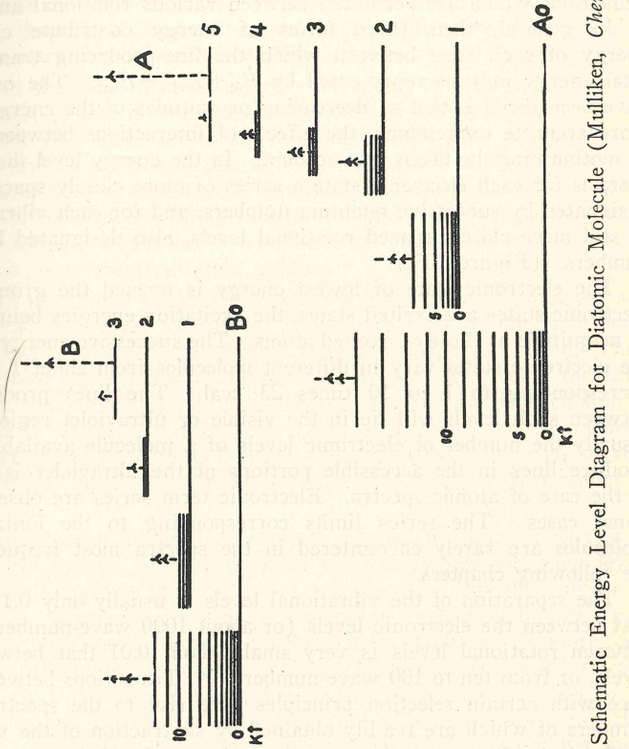


FIGURE 105. Schematic Energy Level Diagram for Diatomic Molecule (Mulliken, *Chemical Reviews*).

states of the molecule might account for the energy differences corresponding to the lines in the far infrared spectra of diatomic molecules. Schwarzschild[5] employed a series of integral quantum numbers in an expression by which the quantized moment of momentum of the rotating molecule could be used in calculating the wave-numbers of the various lines corresponding to shifts between rotational states. Heurlinger[6] introduced vibrational quantum numbers for dealing in a similar manner with the to-and-fro oscillations of the nuclei with respect to each other. Kratzer[7] developed the theory of the vibrations of an anharmonic oscillator in terms of the approximation that the motions of rotation and vibration do not mutually influence each other. He also employed selection principles analogous to those employed in atomic spectra for the restriction of the transitions which are permitted between various rotational and vibrational states.

In general, then, three forms of energy contribute chiefly to the total energy of each state between which the line-producing transitions occur. The total energy may be represented by $E_{el}+E_{vib}+E_{rot}$. The order in which these have been listed is that of decreasing magnitudes of the energy contributions. In more accurate expressions, the effects of interactions between the various forms of motion must be taken into account. In the energy level diagram of a molecule there is for each electronic state a series of more closely spaced vibrational states designated by successive quantum numbers, and for each vibrational level a series of still more closely spaced rotational levels, also designated by integral quantum numbers. (Figure 105.)

The electronic state of lowest energy is termed the ground state; the other electronic states are excited states, the excitation energies being of the same order of magnitude as those of excited atoms. The successive energy increments between the electronic states vary in different molecules from about 1 to 10 electron-volts, corresponding to 1 to 10 times 23 kcal. The lines produced by transitions between such levels will lie in the visible or ultraviolet regions of the spectrum. Usually the number of electronic levels of a molecule available for transitions to produce lines in the accessible portions of the ultraviolet is much smaller than in the case of atomic spectra. Electronic term series are observed only in exceptional cases. The series limits corresponding to the ionization potentials of molecules are rarely encountered in the spectra most frequently referred to in the following chapters.

The separation of the vibrational levels is usually only 0.1 to 0.01 as great as that between the electronic levels (or about 1000 wave-numbers). The difference between rotational levels is very small, about 0.01 that between the vibrational levels, or from ten to 100 wave-numbers.[7a] Transitions between terms in accordance with certain selection principles give rise to the spectral lines, the wave-numbers of which are readily obtained by subtraction of the values of the energy levels (terms) expressed as wave-numbers. In the most general case in the visible and ultraviolet regions, the lines are due to transitions in which the electronic, vibrational and rotational energies each suffer change. For a given electronic shift, there may be a diversity of simultaneous changes in the vibrational and rotational levels. This accounts for the great number of lines of molecular spectra. Transitions between two electronic levels give rise to a band system and those between other electronic levels to other band systems. Each band in the

[5] Schwarzschild, K., *Preuss. Akad. Wiss., Sitzber.*, 548 (1916).
[6] Heurlinger, T., *Physikal. Z.*, 20, 188 (1919); *Z. Physik*, 1, 84 (1920).
[7] Kratzer, A., *Z. Physik*, 3, 289 (1920).
[7a] In the light molecules, H_2, He_2, LiH, the rotational levels are more widely separated.

series comprising a single band system arises from a shift in the vibrational quantum number superposed upon one and the same shift between electron levels. The many fine lines which make up the structure of each band are determined in analogous fashion by the possible rotational shifts which may accompany the electronic and vibrational shifts which locate the position of the band edge.

Spectra may be encountered in the production of which neither electronic nor vibrational transitions have occurred. Since in these the transitions are exclusively between rotational states, such spectra are called pure rotation spectra. Since the rotational states lie very close together, transitions between them involve the emission or absorption of but very small amounts of energy so that the corresponding rotational lines have very low frequencies and lie far in the infrared. In practice, these lines are observed only in absorption spectra and have been comparatively little studied because of experimental difficulties. During the production of such spectra the molecules are always in the ground electronic state.

The frequencies in the near infrared region correspond to greater energy differences between terms, so that in their production certain transitions between the more widely separated vibrational levels are involved. Each such transition corresponds to a band, and as previously stated, each line within the structure of a given band corresponds to a change in the rotational state as well as that vibrational change which is concerned in the production of every line within that band. These near infrared spectra originating in simultaneous vibrational and rotational transitions are known as rotation-vibration spectra.

In the visible and ultraviolet regions electronic transitions are concerned and are accompanied by simultaneous vibrational transitions each producing a band and by rotational transitions responsible for the lines composing each band. Thus, each line in such a band corresponds to the same electronic shift and to the same vibrational shift, but the vibrational shift is different in the case of each line of each of the other bands. The origin of each band may be located by the frequencies corresponding to vibrational transitions between the zero rotational levels of successive vibrational levels, that is, the frequency is $\nu = \nu_{el} + \nu_{vib}$ corresponding to $\nu_{rot} = 0$.

In the production of near infrared absorption spectra, the limited energy in each absorbed quantum usually suffices to excite but a very few vibration levels so that but a few bands (one to three or four) can appear. But the number of bands in the visible or ultraviolet regions accompanying each electron shift may be much greater, the vibrational quantum numbers may reach ten or more, and the spectra are accordingly much more complex. Molecules composed of two like atoms (H_2, N_2, etc.) exhibit no absorption in the infrared from 100μ to 1μ and lack pure rotation and rotation-vibration spectra. This does not mean that such molecules lack rotational or vibrational energy but indicates only that these symmetrical molecules lack the electrical moments whose existence is a prerequisite for interaction with electromagnetic radiations. When an electronic excitation has been brought about in such a symmetrical molecule, the resultant electronic structure is such as to make the molecule an electrical dipole capable of interacting with electromagnetic waves. For this reason the type of information yielded for heteropolar molecules by infrared rotation-vibration spectra can be obtained in the case of homopolar molecules only in the visible or ultraviolet regions. Even then, the spectra of these bands will be due to the transitions between rotational and vibrational states of the electronically excited molecules rather than that of the molecules in the ground electronic state. Information

regarding the vibrational and rotational levels of homopolar molecules may, however, be derived from studies of the Raman spectra to which brief reference is made in another section.

In general, the far infrared spectrum yields information about the rotational levels in the ground or electronically unexcited state of heteropolar molecules, and the near infrared region does the same for both the rotational and the vibrational levels. Similar information regarding the vibrational levels of electronically excited molecules is obtained from the series arrangement of the visible and ultraviolet bands; fine structure studies of the individual bands in these regions give information about the rotational term separations. To obtain similar data for the ground state it would be necessary to utilize the experimentally more difficultly accessible infrared spectra, or else to use the newer Raman spectra.

Pure Rotation Bands and the Information They Yield

Spectra resulting from transitions between purely rotational states lie in the far infrared from 50μ to 200μ. Those of diatomic molecules consist of a series of equidistant lines, the separation of which yields valuable information regarding the molecular dimensions.

In a diatomic molecule rotating as a whole about an axis through its center of gravity, one of the three possibilities for rotation has a zero moment of inertia and the other two are equal. There is accordingly only one series of rotational quantized energy states which needs to be considered. The energies of the states are determined by the integral quantum numbers and by the moment of inertia of the molecule. This latter in turn is dependent upon the masses of the atoms composing the molecule and their separation. It is thus evident that, since the masses of the atoms are known, measurement of the energies of the various rotational states should furnish important information in regard to the sizes of the molecules. The manner in which this may be done lies beyond the scope of this book. This topic is mentioned merely to indicate the nature of the information it is possible to derive from band spectra.

The wave-number of a rotational state is given by $\frac{h}{8\pi^2 I} m(m+1)$ in which m may be zero or an integer and I is the moment of inertia. A selection rule states that the quantum number m may change by only one in a transition producing a line. Therefore, the wave-number of a line in this spectrum is given by the difference between two such terms, one having an m value one greater than the other. The expression for a given line reduces to $\nu = \frac{h}{4\pi^2 I} m$. The wave-number separation of a series of such lines corresponding to successive integral values of m thus permits of a calculation of I, the moment of inertia of the molecule. From the moment of inertia and the masses of the atoms, it is then possible to calculate the radius of the separation of the atomic nuclei. In exact work, a slight correction is required for a change in I due to centrifugal force in the higher rotational states.

The Vibration-Rotation Bands

Absorption of a larger near infrared quantum produces a transition between vibrational states and is responsible for the production of a band. The corresponding wave-length, if there were no accompanying rotation, would locate the position of the band and would be called the zero line. Actually the absorption spectra of diatomic molecules fail to show this line since a selection principle requires that there be a rotational shift accompanying each vibrational transition. As previously stated, the series of lines composing the band is caused by a series of

simultaneous rotational transitions. The expression for the frequency of each of the lines of a band is given by

$$\nu = \nu_0 + \frac{h}{4\pi^2 I} m$$

in which ν_0 locates the origin of the band and the second term accounts for the effect of the rotational transition. As the rotational quantum number may either increase or decrease by one, the lines corresponding to transitions from each initial rotational state will be located on each side of ν_0. The impression given by the band as a whole is that of two bands each composed of a number of sharp lines, the separation of which is similar to that of the lines of a pure rotation spectrum. The separation of the lines composing a band gives evidence regarding the rotational quanta and, as has been shown in the case of pure rotation spectra, from these much can be learned of the size and shape of the absorbing molecules.

The lines composing a band may be classified into two groups or branches. One series occurring on the long-wave side of the origin has the second term negative in the expression just discussed and is called the negative or P branch. A series in which m is positive occurs on the short-wave side of the origin and is called the positive or R branch. Transitions in which m does not change would give rise to a third branch called the zero or Q branch. Since they would violate the selection principle, the Q branch is usually lacking in the rotation-vibration spectra of the diatomic molecules, but is encountered in the spectra of polyatomic molecules as well as generally in electronic band spectra.

In the earlier attempts to interpret the successive bands in a vibration-rotation spectrum, the diatomic molecule was treated as an harmonic oscillator the vibrational states of which were quantized. The energy in a given state was denoted by $E_v = h\omega(v + \frac{1}{2})$, neglecting the contribution due to rotation. The necessity for the use of $\frac{1}{2}$ was found empirically, but has since been justified on theoretical grounds which cannot be here discussed. ω is the fundamental frequency of vibration of the nuclei and v is a quantum number which may be zero or an integer. When v is zero (the so-called vibrationless state) the molecule still possesses the vibrational energy $+\frac{1}{2}h\omega$. Successive integral values of v then give the successive vibrational states and transitions between these the zero lines of successive bands. To obtain the structure of the band use must be made of the more complete expression containing the rotational contribution to the energy state. From this theory but one infrared band would be expected. Its zero line is given by the fundamental frequency and its structure by the rotational effects. No matter whether the vibrational transition is from $v=0$ to $v=1$ or from $v=3$ to $v=4$, the zero line might be expected to be in the same position. (If the electronic structure of the molecule be altered as in the case of band spectra in the visible and ultraviolet regions, the fundamental frequency is, however, altered.) Actually, however, the diatomic molecule is not a true harmonic oscillator; the binding between the atoms is not elastic since the attractive force between them does not increase to infinity as they are more and more widely separated.

In the harmonic oscillator the restoring force K per cm. displacement z of the atoms from their equilibrium separation is proportional to this displacement.

$$K = -a\,z$$

The true frequency is related to a by the expression

$$\text{Frequency} = \nu c = \tfrac{1}{2\pi}\sqrt{\frac{a}{\mu}}$$

in which c is the velocity of light, ν the wave-number of the fundamental frequency and μ the "reduced mass" of the molecule, by which is meant the product of the masses of the two atoms divided by their sum. In the case of the non-harmonic oscillator, it is necessary to employ a power series in writing the binding force between the atoms,

$$K = -az + bz^2 + cz^3 \ldots$$

This means that higher powers, at least the second, of the vibrational quantum number must be employed in expressing the vibrational term wave-numbers.

$$\nu = (v + \tfrac{1}{2})\omega_0 - (v + \tfrac{1}{2})^2 x\omega_0.$$

Here x is a factor for the anharmonicity of the binding and determined by the cofficients in the power series written above. The differences between successive terms responsible for the origin of the bands are thus equal to $\omega - 2x\omega(v + 1)$. This makes it evident that several bands corresponding to different values of n may appear in a system. From this relation it appears that the separation of the successive bands of a system tends to decrease as the quantum number attains high values. Actually only a few bands are usually encountered in the near infrared spectra.

In polyatomic molecules,[8] there may be several modes of vibration, including deformation vibrations in non-linear molecules. The resultant band spectra produced as a result of the interplay of these various forms of motion may be quite complex. The near infrared spectrum of ammonia, for example, contains 13 bands. In each series of bands those involving transitions between states of higher quantum numbers decrease rapidly in intensity, so that those capable of yielding accurate measurements are relatively few.

Raman Spectra. Much of the information regarding the vibration frequencies of various linkages can be more readily obtained by observations of their effects upon the scattering of visible and ultraviolet monochromatic radiations: in 1928, Raman[9] observed that the ordinary radiation scattered by molecules in dust-free liquids or gases contains, besides the radiation of the same wave-length as the incident light, still other wave-lengths, usually of lower frequencies, together with some lines of lower intensity but of higher frequencies. The wave-numbers corresponding to the shifts of the frequency of the new lines in the scattered radiation from the frequency of the incident radiation are in general related to the frequencies of infrared bands. The importance of this new tool led to a large number of investigations of a wide variety of substances, solids, liquids, gases and solutions. The information secured with Raman spectra on the structure of organic molecules has been reviewed by Dadieu and Kohlrausch.[10]

The discussion of the physical aspects of the Raman effect lies beyond the scope of this work. Its value consists in part in the fact that it permits a determination of frequencies of vibration of molecules in their ground states and in part in that it is also applicable to homopolar molecules.

Electronic Band Spectra

Electronic excitation is the chief alteration produced in a molecule by the absorption of visible or ultraviolet radations. The early development of the theory was due to Heurlinger, to Lenz[11] and to Kratzer.[12]

All lines accompanying a single given electronic transition belong to the same band system. The various bands within the system are ascribed to the accompanying vibrational transitions and the lines within the bands to the rotational shifts. Although but a few bands of the ground electronic state can be observed in infrared spectra, in the visible and ultraviolet band spectra a larger number of bands corresponding to quantum numbers as high as ten or twenty may be observed. In some cases it is possible to follow the asymptotic convergence of the successive bands toward a limit. This implies the gradual disappearance of the binding force between the atoms on increased separation during vibrations.

The considerations relating the various bands (taken from their zero lines) to each other are similar to those in the case of the infrared vibration-rotation spectra, and similarly, the structure of each band is analogous to that of the infrared band, a Q branch being also usually present. The close packing of the lines near the head of a band often makes it very difficult to disentangle the band structure. During the electronic shift there is a change in the structure of the molecule which involves a change in its moment of inertia.

Each line is given by an expression which involves a term for the contribution due to the electron shift, one for the vibration shift (together with a second power correcting term for the anharmonicity of the oscillator) and a term for the rotational shift together with a second power term introduced because of the change of the moment of inertia during the electronic shift. The structure of the band is thus given by $\nu = \nu_{el+os} + bm \pm cm^2$, in which b is approximately $h/4\pi^2 I$, the I referring to the lower electronic state. The constant c (about $0.1b$) may be positive or negative and corrects for the change in the moment of inertia. When negative, as m increases, it yields the R branch. As cm^2 grows faster than bm, the lines crowd together. At some value of m, cm^2 exceeds bm (the head of the band) so that with larger values of m there results a decreasing series with increasing spacings of the lines. The position of the head of the band depends on the ratio of b to c. When c is negative, the head occurs on the high frequency side of the origin. Negative values of m yield the P branch; these lines will gradually decrease in frequency and have greater separation as m increases. The intensities of the lines decrease and the band shades off on the lower frequency side. The Q branch lies between the R and P branches.

The complete interpretation of the band spectrum of a compound is a matter of great difficulty largely because of the great number of energy states which may be possessed by a molecule. Even the classification of the lines into the bands, series of bands, and electronic band systems is rendered very difficult because of overlapping of the various structural units and because the electronic energy states, like those of atomic spectra, exhibit multiplicity. The early development of the theory[13] was based upon a formal analogy between line and band spectra, the electronic terms of each involving various quantum numbers; similar selection principles were used. The systematization of the relations between the electronic structures of diatomic molecules and the nature of their band spectra is due in large part to Mulliken,[14] who proposed a notation for designating the state of each electron and of the molecule as a whole.[15]

[8] See Villars, D. S., *Chem. Rev.*, **11**, 369 (1932); Dennison, D. M., *Rev. Modern Physics*, 3, 280 (1931).

[9] Raman, C. V., and Krishnan, K. S., *Nature*, **121**, 501, 619 (1928); *Indian J. Physics*, 2, 387 (1928); **6**, 263 (1931); *Trans. Faraday Soc.*, **25**, 781 (1929). The effect was independently discovered by Landsberg and Mandelstam, *Naturwiss.*, **16**, 557 (1928).

[10] Dadieu, A., and Kohlrausch, K. W. F., *Ber.*, **63B**, 251 (1930); translation by Hollaender, A., *J. Opt. Soc. Am.*, **21**, 286 (1931). Hibben, J. H., "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, 1939.

[11] Lenz, W., *Verh. deutsch. Phys. Ges.*, **21**, 632 (1919).

[12] Kratzer, A., *Ann. Phys.*, **67**, 127 (1922); **71**, 72 (1923).

[13] Mecke, R., *Physik. Z.*, **26**, 217 (1925); *Z. Physik*, **28**, 261 (1924); **32**, 823 (1925); **31**, 709 (1925); **36**, 795 (1926); *Naturwiss.*, **13**, 698 (1925). Hund, F., *Z. Physik*, **36**, 657 (1926); **51**, 759 (1928); Birge, R. T., *Nature*, **117**, 300 (1926).

[14] Mulliken, R. S., *Proc. Nat. Acad. Sci.*, **12**, 144, 151 (1926); *Phys. Rev.*, **29**, 391, 921 (1927); **30**, 138, 150, 175, 785 (1927); **32**, 186, 761 (1928); **33**, 730 (1929).

[15] Other important contributions were made by Birge, R. T., *Phys. Rev.*, **27**, 245 (1926); Kemble, E. C., *Z. Physik*, **35**, 286 (1925); *Proc. Nat. Acad. Sci.*, **10**, 274 (1924); *Phys. Rev.*, **25**, 1 (1925); Kratzer, A., *Z. Physik*, **33**, 144 (1925). The subject is one for a specialist.

In analogy with the S, P, D. . . . terms for atoms there are recognized Σ, Π, Δ terms for molecules. These correspond to the successive values of a quantum number Λ (0, 1, 2). While in the atom, the orbital number L gives the resultant orbital angular momentum of all the electrons, in the molecule the presence of the two nuclei introduces certain complications. But, since the internuclear line is still an axis of symmetry, the component of the orbital angular momentum along this line remains a constant, which may be measured in units of $h/2\pi$. As in the case of the atom, the resultant spin angular momentum of all the electrons serves as another quantum number S. Dependent upon its value (0, ½, 1 . . .) there may be singlet, doublet, triplet states of the molecule. The multiplicity is given by $2S+1$ and is denoted in writing a term by an upper left-hand index before the term symbol, which is derived from the value of Λ. The $^2\Sigma$ represents a state with $\Lambda=0$, $S=\frac{1}{2}$, a $^1\Pi$ term a state with $\Lambda=1$, $S=0$, and a $^3\Delta$ term a state with $\Lambda=2$, $S=1$. As with atoms, S is integral or half-integral depending on whether the total number of electrons in the molecule is even or odd. The multiplicity is even for uneven electron numbers and uneven for even electrons. Other features of term designations may be found in specialized treatises.

It is unnecessary to discuss here the various selection principles which have been given to account for the relative frequencies of the transitions between various molecular energy states. Much is known in regard to the lives of the excited states, but the methods by which these may be calculated by means of the Schrödinger equations are primarily of interest to the specialist. For electron transitions in the wave-number range 10^4-10^5 cm.$^{-1}$, the excited states have a life of about 10^{-8} second. For transitions in vibration frequencies in the range of 10^2-10^3 cm.$^{-1}$ the life of the excited states is of the order of 0.01 second. The lives of rotational states may be even longer.

Account must also be taken of the existence of the spins of the nuclei, information about which is yielded by studies of the alternating intensities of the lines in a band of a homopolar molecule.[16] If the two spins oppose each other, the molecule is called symmetrical and if they are in the same direction, it is called antisymmetrical. Wave mechanics indicates the probability of the existence of antisymmetrical hydrogen to be three times that of symmetrical hydrogen. Ordinary hydrogen behaves as a mixture of two gases. The discovery of the existence of this mixture was a spectacular outcome of the work on band spectra. At very low temperatures all of the hydrogen is in the symmetrical form. Bonhoeffer and Harteck have found charcoal to act as a catalyst for the conversion of one form to the other. The two forms have different specific heats and the change in the proportion of the two effected in the presence of the catalyst can be demonstrated by a change in the heat conductance. The antisymmetrical form has been denoted ortho- and the symmetrical form as para-hydrogen. In hydrogen at room temperatures, there is three times as much ortho- as para-hydrogen. The existence of these two forms of hydrogen was predicted by Heisenberg[17] and by Hund.[18] Bonhoeffer and Harteck later made detailed studies of the physical properties of the two forms.[19] Adsorption on charcoal at liquid air temperatures gives practically pure para-hydrogen.

[16] Mulliken, R. S., *Trans. Faraday Soc.*, **25**, 634 (1929).
[17] Heisenberg, W., *Z. Physik*, **41**, 239 (1927).
[18] Hund, F., *Z. Physik*, **42**, 93 (1928); see also Dennison, D. M., *Proc. Roy. Soc.*, **115**, 483 (1927).
[19] Bonhoeffer, K. F., and Harteck, P., *Naturwiss.*, **17**, 182, 321 (1929); *Z. physik. Chem.*, **4B**, 113 (1929); **5B**, 292 (1929); see also Eucken, A., and Hiller, K., *Ibid.*, **4B**, 142 (1929).

Isotopes in Band Spectra. Since different isotopes of an element have different masses, the momenta of inertia of molecules containing different isotopes should be different. As a result, the bands in the visible or ultraviolet due to molecules some of which have one and others another isotope will be characterized by a duplication of the lines. The bands themselves are also split and superposed.

The existence of isotopes of carbon (13), nitrogen (15), oxygen (17) and of certain other elements were predicted from the data of spectroscopy before they were found by the use of the mass spectrograph of Aston. The oxygen isotope (18) was detected in this manner by Giauque and Johnston in 1929. In the electronic band spectra of isotope mixtures, there is a splitting of the zero position of the bands due to an electronic shift between "vibrationless" states. Its existence implies that the "non-vibrating" molecule is actually in vibration since two isotopic molecules in this state are energetically different. The occurrence of this phenomenon makes certain the existence of a "zero-point" energy of vibration and accounts for the use of $(v+\frac{1}{2})$ in the succession of vibrational terms used in the formulas for the zero lines of bands.

Attempts have been made to effect a separation of isotopes by photochemical means. Kuhn and Martin[20] irradiated phosgene with monochromatic light (2816.179A) obtained from an aluminum arc by the use of filters, and found that the liberated chlorine showed a slight excess of Cl^{35}. Zuber[21] effected a partial separation of the isotopes of mercury by photoöxidation by the aid of a filter which transmitted only the hyperfine components of a spectral line capable of exciting only certain isotopes.

This brief review of the nature and structure of molecular spectra is intended only to serve as an indication of their importance in yielding data of fundamental significance to many branches of chemistry. In the detailed discussion of photochemical reactions in the remainder of the book we shall be concerned with molecular spectra only in so far as they yield information regarding the stability of a photochemically reacting molecule. When by the absorption of energy a molecule is raised to successively higher and higher vibrational states, it may be made to dissociate when the requisite amount of energy has been absorbed. Usually, however, for a vibrational state producing dissociation to be obtained by a molecule absorbing in its ground state, quanta great enough to produce an electronic transition are required. The electron shift alters the binding of the atoms in such a manner that the excited molecule upon the simultaneous acquisition of the requisite amount of energy may be raised to a vibrational state which leads to its dissociation. This is the most frequently occurring primary process in photochemical reactions. The applications of band spectral data to the interpretation of photochemical processes will be considered in more detail in the following chapter.

The following are sources of information on band spectra for readers desirous of obtaining a more thorough discussion, including the mathematical treatment, of band spectra.

Books

Kemble, E. C., Birge, R. T., Colby, W. F., Loomis, F. W., and Page, L., *Report of the Committee on Radiation in Gases of the National Research Council*, **11**, Pt. 3, 1 (1926).

Jevons, W., "Report on Band Spectra of Diatomic Molecules," Cambridge University Press, **1933**.

[20] Kuhn, W., and Martin, H., *Naturwiss.*, **20**, 772 (1932); *Z. physik. Chem.*, **21B**, 93 (1933).
[21] Zuber, K., *Nature*, **136**, 796 (1935); *Helv. Phys. Acta*, **9**, 285 (1936).

Kronig, R. DeL., "Band Spectra and Molecular Spectra," The Macmillan Company, New York, 1931.

Ruark, A. E., and Urey, H. C., "Atoms, Molecules and Quanta," McGraw-Hill Book Company, Inc., New York, 1930.

Sommerfeld, A., "Atomic Structure and Spectral Lines," translation by H. Brose, E. P. Dutton and Company, Inc., New York, 1935.

Baly, E. C. C., "Spectroscopy," III, Chapter IV, Longmans, Green and Co., London, 1924.

Griffith, R. O., and McKeown, A., "Photo Processes in Gaseous and Liquid Systems," Longmans, Green and Co., London, 1929.

Sponer, H., "Molekül Spektren und Ihre Anwendung auf Chemische Probleme," 2 vols., J. Springer, Berlin, 1935–6.

Herzberg, G., "Molecular Spectra and Molecular Structure," Prentice-Hall, Inc., New York, 1939.

Review Articles

Mulliken, R. S., *Chem. Rev.*, **6**, 503 (1929); *Rev. Modern Physics*, **4**, 1 (1932).
Rabinowitsch, E., *Z. Elektrochem.*, **37**, 91 (1931); **38**, 370 (1932).
Villars, D. S., *Chem. Rev.*, **11**, 369 (1932).
Hund, F., *Z. Elektrochem.*, **36**, 596 (1930); *Physikal. Z.*, **28**, 779 (1927).
Urey, H. C., *Ind. Eng. Chem.*, **23**, 1241 (1931).
Mulliken, R. S., *J. Phys. Chem.*, **41**, 5 (1937).
Noyes, W. A., Jr., *J. Phys. Chem.*, **41**, 81 (1937).
Weizel, W., *Physikal. Z.*, **34**, 425 (1933).
Johnson, R. C., *Sci. Progress*, **22**, 231 (1927).
Schofield, R. K., *Sci. Progress*, **24**, 572 (1930).
Kronig, R. DeL., *Physica*, **9**, 81 (1929).
Symposium of the Faraday Soc., *Trans. Faraday Soc.*, **25** (1929).

Chapter 14

Spectroscopic Evidence for Dissociation as the Primary Photochemical Process

It is now necessary to consider the manner in which the stability of a molecule sets a limit to the amount of vibrational energy which it can absorb and still remain a molecule. The guiding principle is that a molecule either in the ground state or, as is more commonly the case, in one of its electronically excited states, cannot absorb more vibrational energy than corresponds to its work of dissociation without falling apart into atoms or, if it is a polyatomic molecule, into atoms and free radicals, or two free radicals.

The present viewpoint may be said to have taken its origin from the work of Franck on the dissociation of molecules by electron impact. Blackett and Franck[1] found experimentally that a hydrogen molecule can be decomposed by one collision, a continuous spectrum appearing at the same time. They suggested that the first effect of the collision is to raise an electron suddenly to a higher level. In this new configuration there is a large repulsion between the nuclei great enough to split the molecule into a normal atom and an excited one, both atoms having high velocity. Franck[2] extended the concepts derived from these experiments to an interpretation of photochemical dissociation. In this case the excitation of the molecule and its resultant dissociation are produced, not by a collision with a rapidly moving electron, but the absorption of a quantum $h\nu$ equal to or greater than the work of dissociation of the molecule. If the separation of the atoms during a vibration becomes great enough to overcome the binding force between the nuclei, the atoms may fall apart. It was, however, well known that quantities of energy larger than the work of dissociation may be absorbed by molecules without destroying them. Franck explained this by showing that in such cases not all of the absorbed energy is available as vibrational energy. Instead, a large part of the absorbed energy is consumed in raising the electron system to a higher quantum state, the remaining energy being available only for changing the vibrational and rotational states. Since the rotational quantum is but small, the effects of a change in rotational energy may be neglected. The problem may thus be reduced to that of the stability of the molecule in its various electronically excited states with respect to vibrational energy. Franck prepared potential energy diagrams in which the potential energies of the vibrating atoms are plotted as ordinates against the separation of the atoms as abscissae. Before considering these curves and their relation to spectroscopy, it may be simpler to consider the manner in which molecular spectra indicate the occurrence of dissociation.

Interpretations of Continuous Regions in Spectra

In Chapter 2, it was stated that in atomic spectra the lines of a series converge to a limit. On the short-wave side of this limit the spectrum is continuous. This

[1] Blackett, P. M. S., and Franck, J., *Z. Physik*, **34**, 389 (1925).
[2] Franck, J., *Trans. Faraday Soc.*, **21**, 536 (1926).

was interpreted as indicating the separation of an electron from an atom, the latter thereby becoming an ion. The absorption is continuous rather than discrete because the motion of the electron on leaving the atom is not quantized. The velocities with which the electrons are ejected from the various atoms present in the absorbing gas vary continuously and are not limited to definite values. Non-quantized energy levels correspond to non-periodic movements. During the process of ionization the electron changes its motion from a periodic one in an orbit to a non-periodic one in the hyperbolic path which carries it away from the ion. When at a sufficient distance from the ion the electron moves in practically a straight line. It may have any kinetic energy depending upon the amount by which the particular wave-length absorbed exceeded in energy the amount required for the ionization. Since in the light producing the ionization there may be present quanta varying almost continuously in magnitude, atoms absorbing any quantum, A, more than sufficient to produce ionization, will give kinetic energy to the electrons and the ions corresponding to the excess energy. But atoms ionized by quanta corresponding to a wave-length infinitesimally near to that corresponding to A will produce electrons having an infinitesimally greater kinetic energy. Thus when a wave-length band of energy greater than that required to produce ionization is absorbed, the electrons produced will be endowed with continuously varying kinetic energies. Thus it is that in atomic line spectra a continuous region beginning at the convergence limit of a series marks the frequency which corresponds to the work of ionization.

A similar ionization of a diatomic molecule can occur but is rarely of photochemical significance. Before ionization of the molecule could be attained, the energies required would be usually more than sufficient to break the molecule into atoms. The effect of dissociation upon the appearance of the spectrum is, however, similar to that of ionization.

Before dissociation, the atoms of a molecule are vibrating to and fro on the line joining their nuclei. With increasing increments of vibrational energy they are separated more and more widely at each oscillation. When the separation becomes great enough the restoring force between the atoms becomes reduced to zero, the vibratory motion between the atoms ceases, and the atoms become separated. Since the kinetic energies with which the atoms move are not quantized, the absorption spectrum becomes continuous at wave-lengths shorter than that which corresponds energetically to dissociation. It must be noted that the molecule which dissociates rarely is in its ground electronic state. Therefore, the energy of dissociation need not be expected to coincide with that required for thermal dissociation. The wave-length at which the spectrum becomes continuous represents the convergence limit of a series of vibrational states of the dissociating molecule in the electronic state from which dissociation occurs. Dymond[3] found a continuous range in the absorption spectrum of iodine vapor. Bonhoeffer and Steiner,[4] as well as Tingey and Gerke,[5] reported a continuous region in the absorption spectrum of hydriodic acid.[6]

Corroboratory evidence for the theory that a region of continuous absorption implies dissociation was soon forthcoming from measurements of the fluorescence of vapors at low pressures. It was stated in Chapter 12 that when the pressure is low, so that collisions are rare, excited molecules re-emit their excitation energy

[3] Dymond, E. G., *Z. Physik*, **34**, 553 (1925).
[4] Bonhoeffer, K. F., and Steiner, W., *Z. physik. Chem.*, **122**, 287 (1926).
[5] Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, **48**, 1838 (1926).
[6] See also Leifson, S. W., *Astrophys. J.*, **43**, 73 (1926), for other gases.

as fluorescence after a period of about 10^{-8} second. Dymond,[7] observed this fluorescence in iodine vapor excited by the absorption of long wave-lengths. But when the absorbed light had only wave-lengths less than about 5000A, the region in which continuous absorption begins, this fluorescence could no longer be observed, an indication that the molecules were no longer present and so could not reëmit their energy of excitation. Similar observations were reported by Bonhoeffer and Farkas.[8] The fluorescence test for dissociation is limited to very low pressures of gas or vapor, since when the pressure is high deactivating collisions become frequent and might remove the excitation energy and so extinguish fluorescence even though dissociation by direct absorption did not occur. Errors due to the emission of radiation as a result of the recombination of atoms to form molecules rarely arise, since, as has been noted in Chapter 13, free atoms rarely combine to form molecules with the emission of their excess energy.[9]

Other types of experimental evidence have been advanced to support the theory of direct dissociation. One method employs identification of the resulting free atoms by their characteristic absorption lines. Iodine atoms absorb the 1830.4A line strongly, but iodine molecules do not. Turner found that iodine vapor when irradiated by a carbon arc shows an increased absorption of this line, indicating the presence of iodine atoms. Senftleben[10] demonstrated that excited mercury atoms can dissociate hydrogen. The dissociation was measured by change in the heat conductivity of the gas by a method dependent upon a change in resistance of a wire kept in the gas. With Germer, he extended the method to show the direct dissociation of the halogens on irradiation. That the energy absorbed in excess of that required for dissociation appears as kinetic energy of the atoms was demonstrated by Hogness and Franck[11] for the case of sodium iodide vapor at 650°C. The dissociation yields a normal iodine atom and an excited sodium atom, the latter spontaneously emitting the sodium D line. The Döppler effect (shift in wave-length of the light from a moving source) was utilized to secure information as to the kinetic energy of the sodium atom when produced by the dissociation of the sodium iodide vapor by various wave-lengths within the region of continuous absorption. The Döppler effect was measured by the relative transmission of the emitted light by a layer of sodium vapor, which can only absorb the D line. When the dissociation was effected by a silver arc giving effective intense radiation only in the neighborhood of 2450A, 80 per cent of the emitted light was absorbed by sodium vapor. When the dissociating source was a cadmium arc emitting shorter wave-lengths (capable of giving more kinetic energy to the dissociated atoms), only 76 per cent of the emitted light was absorbed by the sodium vapor. With the still shorter radiations of a zinc arc (2139-2026A), the Döppler effect was increased to such an extent that but 50 per cent of the emitted light was absorbed. In this way it could be shown that the kinetic energy of the liberated atoms increases as the frequency of the irradiating light is increased beyond a limit corresponding to 2450A.

Polyatomic molecules, as water, methanol and methyl cyanide, when decomposed by radiations within the Schumann region give rise to excited free radicals, such as OH and CH, which spontaneously emit characteristic bands.[12] Still

[7] Dymond, E. G., *loc. cit.*
[8] Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **132**, 235 (1928).
[9] Kondratjew, V., and Leipunskiĭ, A., *Z. Physik*, **50**, 366 (1928); **56**, 353 (1929); *Trans. Faraday Soc.*, **25**, 736 (1929).
[10] Senftleben, H., *Z. Physik*, **32**, 922 (1925).
[11] Hogness, T. R., and Franck, J., *Z. Physik*, **44**, 26 (1927).
[12] Terenin, A., and Neuĭmin, H., *Nature*, **134**, 255 (1934).

other lines of direct evidence for the liberation of free atoms and free radicals, such as the conversion of para-hydrogen to ortho-hydrogen, and the effects of free radicals on metallic films, have been advanced. There is now general agreement that photodissociation in a single act of absorption may occur as a result of a primary absorption process. In the case of the reactions of gases which contain a small number of atoms, the nature of the absorption curve of the gas affords a reliable criterion for the occurrence of dissociation. When the absorption lies within a continuous region, the result is dissociation. In the case of very complex gaseous molecules containing more than about six atoms, the evidence from spectroscopy is less definite, since the banded region is not well marked in their spectra. In reactions conducted in solution, absorption curves afford little or no evidence regarding the nature of the primary process. (See Chapter 20.)

Franck's Potential Energy Curves

In his Faraday Society paper, Franck visualized the distinction between the dissociation of excited states of molecules and their stability in the ground state by the aid of the potential energy diagrams reproduced in Figure 106. In each

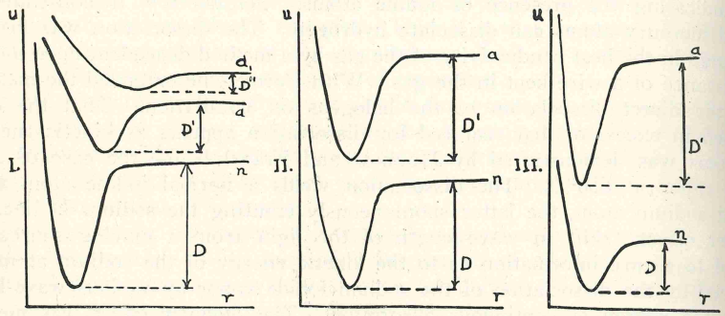


Figure 106. Potential Energy Diagrams of Franck *(Transactions of the Faraday Society).*

of the three diagrams, the lower curve applies to the ground state of a molecule and the upper curve or curves to various electronically excited states. The differences between the upper and lower curves are intended to illustrate the manner in which the change in electron configuration alters the stability of the molecules. To understand the nature of a single one of these curves, it is simplest to consider first the discussion of the meaning of the curves as described by Rabinowitsch in a paper on the interpretation of band spectra.[13]

It was stated in Chapter 13 that for the pure harmonic oscillator,

$$K = -az$$

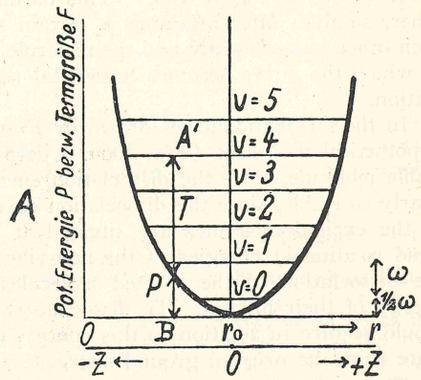
This means that the restoring force during an harmonic oscillation is proportional to the displacement z on either side of an equilibrium separation of the atoms of a diatomic molecule. Integration yields the potential energy:

$$P = \frac{az^2}{2}$$

[13] Rabinowitsch, E., *Z. Elektrochem,* **37**, 91, 370 (1931).

This is the equation of a parabola (Figure 107) with its two branches meeting at $z=0$, the equilibrium distance between the nuclei, r_0, being measured from the origin. During a vibration from the point of greatest separation of the atoms, the potential energy follows the course of the curve. When the atoms are far apart the attractive forces of valence require that there be a great potential energy. As they move toward each other, this becomes transformed into kinetic energy. At the equilibrium point the potential energy is zero, all the energy being kinetic. As the kinetic energy carries the atoms closer together, the energy again becomes potential because the repulsive forces of the nuclei tend to keep the atoms from coming together. The position of equilibrium (determined as described in the previous chapter from rotational term separations) depends upon the relative magnitudes of the attractive and repulsive forces of the atoms. If the molecule possesses energy denoted by A on the ordinate, a line parallel to the abscissa

Figure 107.
Potential Curve and Vibrational Terms for Harmonic Vibrator (Rabinowitsch, *Z. Electrochemie*).
Z = Elongation
r = nuclear separation
$Z = r - r_0$



drawn through A would cut the curve in two places. These determine the distances between the atoms at the extremes of its vibrations when it possesses this amount of potential energy. At these distances from the equilibrium position the total energy of the molecule is potential; there is no kinetic energy. The atoms, changing their directions, are momentarily at rest with respect to each other. At any other distance between the atoms, as for example, at A', part of the energy is potential and part kinetic. By dropping a perpendicular from this point to the abscissa, it is evident that the relative fraction which is potential is given by the ratio $BP:BA'$. Since the vibrational states of the molecule are quantized, the potential energies of the molecule in its permitted states are obtained by drawing a series of equally spaced lines parallel to the abscissa. The extremes of separation of the atoms in each of these vibrational states are given by the points at which each of these lines cuts the curve. The equal spacing of the lines corresponds to successive integral quantum numbers.

It is to be especially noted that the first of these, the so-called "vibrationless state" is so drawn as to indicate that even in it the molecule is vibrating with one-half the energy corresponding to its fundamental frequency. It may be recalled that account was taken of this "zero-point energy" in the equation for expressing the wave numbers of vibration band zero lines in terms of a transition between states. (Chapter 13.)

Since real molecules are not harmonic oscillators, certain changes must be made in the form of the potential energy curve, which nevertheless retains its parabolic form near the equilibrium point. The value of x, the anharmonicity factor in the expression for a vibrational term $F\nu = (v+\frac{1}{2})\omega - (v+\frac{1}{2})^2 x\omega$ yields the deviation from the ideal curve to a first approximation. The deviations really result from the necessity for the use of terms in higher powers in the expression for the force of attraction of the oscillator. The effects of the deviations from harmonic oscillations are such as to make the repulsive forces increase more rapidly than linearly as the atoms approach each other, so that the left branch of the curve must be steeper than that of a true parabola. The attractive force no longer increases regularly with the separation. Instead, it attains a maximum at a certain distance of separation of the atoms, after which it becomes smaller and the right-hand branch of the curve changes direction, and finally, at a certain separation of the atoms asymptotically becomes parallel to the abscissa. (See the lower curves of Figure 106.) This means that the atoms no longer attract each other, so that, after attaining a certain separation, they may move away from each other independently and the molecule is dissociated. The value of the energy at which the curve becomes horizontal represents the energy required for dissociation.

In the schematic curves drawn by Franck to illustrate the behavior of various hypothetical molecules (Fig. 106), a deep curve such as I(normal), represents a stable molecule, since the dissociation energy is great. One such as III n is not nearly so stable, since the dissociation energy is less. The minima for the curves of the excited molecules are situated at heights which represent the electronic (and rotational) energies of the non-vibrating electronic states. The energy for the dissociation of the excited molecules is measured only from the potential energy of their minima. To dissociate such an excited molecule photochemically would require in addition to this energy, the energy required to form the excited state from the original ground state.

The various curves illustrate the fact that the excitation of a molecule may either weaken, strengthen or leave unchanged the binding strength of the atoms in the ground state. In I, which shows curves for a molecule in its ground state and in two excited states, a, a', the excitation progressively weakens the binding force. Not only does the energy of dissociation lessen, but since the attractive force is weakened, the separation of the atoms at equilibrium also becomes progressively greater with successive states of excitation. Should the absorption of light which produces the electron transition be represented by drawing a vertical line upwards from the minimum of the curve for the ground state, it would strike the curve for the first excited state at a point indicating a potential energy greater than that (D') required to dissociate the excited molecule. Its atoms would, therefore, fly apart as the vibration traced the curve for the excited state. This type of molecule is encountered in the halogens.

The second part of the figure illustrates the case in which the strength of the binding is independent of the state of excitation.

Section III indicates the case in which the binding is made firmer by excitation, so that the moment of inertia is reduced. Examples are such loosely bound molecules as Cd_2 or Zn_2 for which the heat of dissociation is of the order of less than one kcal.[14]

If in such potential energy curves, the horizontal energy levels for the terms

[14] Winans, J. G., *Nature*, 123, 279 (1929); *Phil. Mag.*, 7, 555 (1929).

corresponding to the successive quantum numbers are drawn in, as in Figure 107 for the harmonic oscillator, the first two or three would be widely and approximately equally spaced. But with successively higher quantum numbers, they become more and more closely spaced (Figure 108), eventually converging at the level at which dissociation occurs. In comparatively few molecular spectra, notably chlorine and iodine, is it possible to trace the convergence of a large number of bands to a limiting frequency which indicates a heat of dissociation.

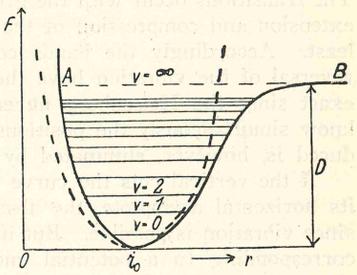


FIGURE 108.

Potential Curve and Vibrational Terms for Anharmonic Vibrations (Rabinowitsch, *Z. Electrochemie*).

In most cases, the bands become weak while still far from the convergence limit and only a limited number of the vibration quanta can be measured directly. Birge and Sponer[15] devised a method of extrapolation to obtain the convergence point.

From the separations of two or more bands, $\Delta\nu = \omega_0(1 - 2vx)$ it is possibly to derive values of the fundamental frequency of the molecule ω_0 and of its anharmonicity x. From these, it was believed that all higher terms might be obtained on the assumption that $\Delta\nu$ is a linear function of v, decreasing as the quantum number increases. At the convergence limit, where $\Delta\nu$ is zero, v is given by $1/2x$. The total energy absorbed is then the integral of ΔF_v between the limits $\nu = 0$ and $\nu = 1/2x$ or $\omega/4x - \omega/2$. To this there must be added the zero-point energy $\omega/2$, so that the heat of dissociation would be equal to $\frac{h\omega}{4x}$. For a graphical solution, $\Delta\nu$ could be plotted against v and extrapolated to $\Delta\nu = 0$, that is to $v = 1/2x$, the area under the curve giving the heat of dissociation.

Application of this method gave results for the heat of dissociation which in many cases were far too high in comparison with values obtained from thermochemical data. It came to be recognized that the equations employed were not strictly valid and that the results were frequently uncertain when but few vibrational bands could be measured and employed in the extrapolation. Near dissociation, the drop in the separation of the vibrational bands often seemed to be accelerated. Birge[16] modified the extrapolation methods. In the method suggested by Birge, ω_v is plotted against the energy of vibration. $E\omega_v = \Sigma\omega_v$. By the use of the improved method the following values for the heats of dissociation of various gases (expressed as electron-volts) were obtained: N_2 9.1, O_2 6.0, NO 6.6, CO 10.3.[17]

Although Franck said little in his Faraday Society paper as to the manner in which the potential energy curves were obtained, the fertility of the concepts they expressed and their value in the interpretation of the various types of photochemical mechanism were quickly appreciated. Condon[18] devised methods of

[15] Birge, R. T., and Sponer, H., *Phys. Rev.*, 28, 259 (1926). Other methods of evaluating heats of dissociation from the long-wave limits of continuous spectra and from predissociation spectra are occasionally employed but cannot be discussed here.

[16] Birge, R. T., *Trans. Faraday Soc.*, 25, 707 (1929).

[17] For the application of the Birge-Sponer method to the determination of the heats of dissociation of organic compounds from their infrared absorption curves, see Ellis, J. W., *Phys. Rev.*, 33, 27 (1929).

[18] Condon, E. U., *Phys. Rev.*, 28, 1182 (1926); 32, 858 (1928); *Proc. Nat. Acad. Sci.*, 13, 462 (1927).

treating the curves more quantitatively from the standpoint of quantum mechanics and used them in explaining the distribution of the intensities of the lines encountered in band spectra. He conceived an electron transition to occur with such extreme rapidity that the light electron moves to its new orbit in a time so brief that the heavier and more slowly moving nuclei undergo practically no change in position or velocity during the transition. This may be indicated by drawing a vertical line joining the curves for the ground and excited states of the molecule. The transitions occur with the greatest probability from the end points of greatest extension and compression of the molecule where the velocities of the atoms are least. Accordingly the bands corresponding to transitions from the points of reversal of the vibration have the greatest intensity. Strictly the method is not exact since the Heisenberg uncertainty principle shows that it is impossible to know simultaneously the positions and velocities of the nuclei. The error introduced is, however, eliminated by treatment by the methods of wave mechanics.

If the vertical cuts the curve for the excited molecule at a point deeper than its horizontal asymptote, the absorption spectrum will be predominantly banded, since vibration is possible. But if the curve for the excited state be cut at a point corresponding to a potential energy greater than that of the asymptote, the absorption will be predominantly continuous.[19] It must be noted that there may be several excited states for which separate curves must be constructed.

It is possible to derive the shape of the Franck-Condon curve for a diatomic molecule from a knowledge of three constants of the molecule, r_0, ω and D by means of an interpolation formula due to Morse,[20]

$$F = D'e^{-2az} - 2D'e^{-az}$$

in which $a = \sqrt{\frac{8\pi^2 c\mu\omega x}{h}} = 0.2454\sqrt{M\omega x}$, μ being the reduced mass in c.g.s. units and M its value in atomic weight units; z is the elongation or the distance from the normal equilibrium nuclear separation r_0, the value of which for a given vibrational quantum number is derived from an analysis of the band spectrum. D' is the heat of dissociation derived thermochemically or by a Birge-Sponer extrapolation.[21] Such curves have been obtained for a large number of molecules and the curves play an essential role in theories regarding thermal reaction rates.[22]

Despite the many difficulties inherent in treating polyatomic molecules, Franck, Sponer and Teller[23] believe that potential energy curves may be profitably employed, at least in qualitive discussions of predissociation.

Excited Atoms Formed by Dissociation

Early efforts to test the dissociation theory by comparing the heats of dissociation determined spectroscopically and thermochemically indicated discrepancies; these for a time led certain workers to prefer the theory that the primary process in a photochemical change is more generally one of molecular excitation.

[19] For quantum mechanical treatments, see Goldstein, L., *Compt. rend.*, **193**, 919 (1931); *J. phys. Radium*, **4**, 123 (1933).

[20] Morse, P. M., *Phys. Rev.*, **34**, 57 (1929).

[21] The calculation of such curves has also been described by Klein, O., *Z. physik*, **76**, 226 (1932). Improved methods have been suggested by others, for which see Sponer, H., "Molekülspektren," J. Springer, Berlin, 1936. Note also Chakravorti, S. K., *Z. Physik*, **109**, 25 (1938).

[22] For further discussion of potential energy curves, see Franck, J., and Sponer, H., *Nachr. Ges. Wiss. Göttingen*, 241 (1928); Visser, G. H., *Chem. Weekblad*, **27**, 237, 380, 390 (1930); Mecke, R., *Physikal. Z.*, **33**, 1 (1932); Noyes, W. A., Jr., *Rev. Modern Physics*, **5**, 280 (1933); Rüdy, R., *Rev. gen. sci.*, **37**, 539 (1926); Heitler, W., and London, F., *Z. Physik*, **44**, 455 (1927); Suguiera, J., *Ibid.*, **45**, 484 (1927); Hylleraas, E., *Ibid.*, **96**, 643 (1935); Finkelnburg, W., *Ibid.*, **99**, 798 (1936).

[23] Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932).

That the atoms formed on dissociation of a molecule need not be in the ground state, but that either one or both might be liberated in an excited state was discussed by Franck. If such should be the case it is evident that the apparent value of the heat of dissociation would be greater than the thermochemical value by the energy of excitation. If then the state of excitation of an atom so formed can be determined and if the energy required to raise the atom to that state from the ground state be known, it should be possible to obtain the heat of dissociation from the ground state of the molecule by subtracting the heat of excitation of the atom from the spectroscopic value for the heat of dissociation of the excited molecule.

Iodine may absorb nearly double its dissociation energy and re-emit it as fluorescence without dissociating. From spectroscopic data of Mecke,[24] Franck stated the convergence limit of the vibrational levels of iodine to lie at 4995A. Figure 103 shows that this corresponds to 56,950 calories. Since the thermochemical value for the heat of dissociation of iodine is only 34,500 calories, it is evident that some other process than dissociation of the ground state must be involved in the photochemical dissociation. From the arc spectrum of the iodine atom, its energy of excitation to the $^2P_{\frac{1}{2}}$ state is found to be 21,650 calories per atom. When this is deducted from 56,950 calories, the remainder, 35,300 cal.,[25] is in good agreement with the thermochemical value. The conclusion is, therefore, that the photochemical dissociation of iodine leads to the production of one normal and one excited atom. Similarly, the convergence limit is 4800A for chlorine and for bromine 5107A, each dissociating into a normal and an excited atom.

A normal molecule rarely suffers photochemical dissociation; when it does two normal atoms usually are formed. Herzberg[26] and Heitler and Herzberg[27] have shown that there are instances in which molecules may yield one normal and one excited atom from the ground state, and two normal atoms from an excited state. This is interpreted to mean that a stable molecule is formed by the union of a normal and an excited atom. Instances are CN, BO, SiN, N_2^+, $(CO)^+$. Still other cases have been discussed by Bengtsson and Hulthén, *e.g.*, CuH.[28]

Homopolar and Heteropolar Molecules

Molecules which, like the alkali halides, yield ions on dissociation from the ground state are called heteropolar or ion-molecules, and those which yield two neutral atoms from the ground state are called homopolar or atom-molecules. In general, atom-molecules such as hydrogen, chlorine, and even such polar ones as silver halides are dissociated from excited states into a normal and an excited atom. Ion-molecules may give both this type of dissociation and one in which only normal state atoms are produced.[29] Franck, Kuhn and Rollefson[30] found the alkali halide vapors to exhibit continuous absorption bands which extend farther toward the red when the temperature and pressure are increased; the position of the maximum absorptions appeared to be independent of these factors. Only one maximum was observed for the chlorides, but there were two for the iodides and bromides. The heats of dissociation of the molecules as calculated from the

[24] Mecke, R., *Ann. Physik*, **71**, 104 (1924).

[25] 35,593 according to Brown, W. G., *Phys. Rev.*, **38**, 709 (1931).

[26] Herzberg, G., *Ann. Physik*, **86**, 189 (1928).

[27] Heitler, W., and Herzberg, G., *Z. Physik*, **53**, 52 (1929).

[28] Bengtsson, E., and Hulthén, E., *Trans. Faraday Soc.*, **25**, 751 (1929).

[29] Sponer, H., *Z. Elektrochem.*, **34**, 483 (1928); Franck, J., and Kuhn, H., *Naturwiss.*, **20**, 923 (1932).

[30] Franck, J., Kuhn, H., and Rollefson, G. K., *Z. Physik*, **43**, 155 (1927).

positions of the longer wave-length continuous bands appeared to be in agreement with thermal heats of dissociation of the salts. Such a conclusion would indicate that it would be possible for ion molecules to be dissociated into two normal atoms.

At low pressures, the vapor of sodium iodide when irradiated with wave-lengths shorter than 2500A emits the D line of sodium.[31] This is proof that the absorption produces an excited sodium atom and an iodine atom. The second series member 3303A only appears when the iodide vapor is irradiated with the 1854-62A aluminum doublet, the energy corresponding to the dissociation energy of the sodium iodide and the excitation of the sodium atom to the 3P state. Since in this process the D line was not emitted, it is not possible that the effects could have been due to an ionization of some sodium vapor possibly present.[32] Similar results were reported by Kondrat'ev [33] for caesium iodide, the dissociation energy of which corresponds to 3.82 volts. The energy required to excite the observed caesium line (4555A) is 2.71 volts. The sum, 6.53 volts, is less than the energy of the aluminum lines 1854 and 1862A which produce the effect, but greater than that of the nickel lines about 2300A, which are ineffective.

In thallium iodide vapor, irradiation with wave-lengths shorter than 2080A leads to the emission of the 3776 and 5351A lines, showing that the dissociation produces thallium in the 2S state; from the result the heat of dissociation into normal atoms would be 61 kcal. per mole.[34] More recently, Terenin and Popov [35] find thallium iodide and bromide to yield thallium and halide ions. Butkov,[36] had previously stated from convergence limits, the heat of dissociation of thallous chloride vapor as 87 kcal. and that of the bromide as 73.1 kcal. Since the decomposition leads to excited atoms, the vapors are atomic compounds.

Neuĭmin [37] finds thallous iodide at 600° and 1 mm. pressure to show two absorption bands with maxima at 3110 and 2510A, diffuse toward the long wave side, corresponding to the potential energy curves for $Tl + Cl^*$ and $Tl^* + Cl$. On irradiating these vapors at 100 mm. by a spark, the photodissociation of the salt yields the lines 3776 and 5351A. These atomic lines are not given by resonance in thallium vapors at these temperatures.[38]

Desai [39] found four regions of continuous absorption to be exhibited by the vapors of rubidium iodide. The first, at 3700A, involves a dissociation into normal atoms with an energy of reaction of 78 kcal. The second at 2900A, leads to the production of a normal rubidium and an excited iodine atom, the third at 2548A, to an excited rubidium and a normal iodine atom, and the fourth at 2150A, to the formation of excited rubidium and iodine atoms.[40]

Sommermeyer [41] agrees that the absorption of alkali halide vapors yields only continuous spectra, but finds that by an excitation method he can observe certain

[31] Kondrat'ev, V., *Z. Physik,* **39,** 191 (1926); Terenin, A., *Ibid.,* **37,** 98 (1926); **44,** 713 (1927); *Naturwiss.,* **15,** 73 (1927).

[32] See also Terenin, A., and Neuĭmin, H., *Physik. Z. Sowjetunion,* **2,** 434 (1932).

[33] Kondrat'ev, V., *loc. cit.*

[34] Terenin, A., *Z. Physik,* **44,** 713 (1927).

[35] Terenin, A., and Popov, B., *Z. Physik,* **75,** 338 (1932).

[36] Butkov, K., *Z. Physik,* **58,** 232 (1929).

[37] Neuĭmin, H., *J. Exp. Theor. Physics, U.S.S.R.,* **4,** 692, 697 (1934); see also Terenin, A., and Popov, B., *Z. Physik,* **75,** 338 (1932).

[38] See also Franck, J. M., *Physik. Z. Sowj.,* **2,** 319 (1932).

[39] Desai, M. S., *Z. Physik,* **85,** 360 (1933).

[40] See also Visser, G. H., and van Heel, A. C. S., *Z. Physik,* **86,** 694 (1933). For alkali fluorides and the heat of dissociation of fluorine, see Desai, M. S., *Bull. Acad. Sci. United Provinces Agra Oudh, India,* **1,** 116 (1931-2); *Chem. Abs.,* **26,** 5842 (1932).

[41] Sommermeyer, K., *Naturwiss.,* **16,** 653 (1928); *Z. Physik,* **56,** 548 (1929).

bands. Their separation was less at the longer wave-lengths and in the ultraviolet they became progressively feebler and finally disappeared. They correspond with the vibration quantum of the normal state of the molecule, which would be strongly excited at the temperatures used (750°). He suggested that the normal electronic state always corresponded with ionic binding, and the excited state with binding by polarization.

The absorption of lithium halide vapors has been studied by Desai [42] who found two absorption regions in the vapors of the bromide and iodide. By the use of the ill-defined long-wave limit of continuous absorption, the latent heat of vaporization of lithium was computed to be 29.6 kcal. per g. atom (using the mean value from data on all the lithium halides). On the assumption that the second absorption region corresponds to dissociation into a normal metal and an excited halogen atom, the excitation potentials of bromine and iodine were computed from the frequency difference between the two absorption limits on the long-wave side, giving for bromine 0.46 volt and for iodine 0.91 volt.

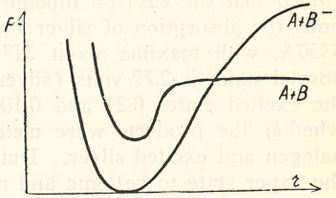


FIGURE 109.

Potential Energy Curves for a Heteropolar Molecule (Rabinowitsch, *Z. Electrochemie*).

Figure 109 illustrates the potential energy curves which characterize a heteropolar molecule. The crossing of the curves is necessary because the energy of a system of two ions must be greater than that of the same two atoms, however excited. The crossing is a point at which the potential energy is the same for a given atomic separation for both the excited and ground states. A molecule at this point may dissociate in either manner so that the molecule cannot be either exclusively homopolar or heteropolar. In some cases the probability of the dissociation following one course exceeds that of its following the other. This is the more likely the greater the energetic separation of the two curves.

It has thus become evident that a simple classification of molecules into heteropolar and homopolar is unnecessary and arbitrary. The view that a given molecule shares the distinguishing features of both types serves to explain the controversy regarding the nature of hydrogen chloride. This was long thought to be heteropolar because of its dissociation into ions in aqueous solutions. Kondrat'ev [43] advanced evidence from the convergence of its infrared bands for a homopolar nature, but Rawlins [44] believed gaseous hydrogen chloride heteropolar because of the constancy of its dielectric constant in a variable magnetic field.[45]

The continuous absorption spectrum of silver iodide vapor closely resembles the spectra of the alkali chlorides.[46] It extends from 3500 to 2400A with a maximum at 3170A. The dissociation results in a normal silver atom and an excited iodine

[42] Desai, M. S., *Bull. Acad. Sci. United Provinces Agra Oudh, India,* **2,** 33 (1932); *Chem. Abs.,* **27,** 2380 (1933).

[43] Kondrat'ev, V., *Z. Physik,* **48,** 583 (1928).

[44] Rawlins, F., *Z. Physik,* **50,** 440 (1928).

[45] See, however, Datta, S., and Chakroborti, B., *Current Sci.,* **3,** 349 (1935).

[46] Franck, J., and Kuhn, H., *Z. Physik,* **43,** 164 (1927).

atom. For dissociation into two normal atoms the absorption band would have to be of much longer wave-length. This conclusion was also confirmed by the fluorescence spectrum excited by irradiating the vapor with the copper line 3274A. The heat of dissociation calculated from the fluorescence spectrum is approximately 54 kcal., whereas that found by measuring the work of dissociation is 47 kcal. This indicates that the dissociation products are two neutral atoms and not two ions for which a heat of dissociation of 140 kcal. would be required. In the vapors of silver bromide the absorption bands lie between 3100 and 3400A and for silver chloride between 3100 and 3300A.[47] The vibration frequency changes only slightly between the initial and final electronic states, the difference decreasing from iodide to chloride. A series of resonance lines was obtained by suitable illumination of the vapors. From these the heat of dissociation of silver bromide is roughly estimated at 2.5 volts, in agreement with the thermochemical value, 2.6. This shows that in the vapor state these molecules are non-polar. The true heats of dissociation are closely related to the constants of the quasi-elastic binding forces obtained from the vibration frequency in the normal state. It is therefore concluded that the electron linkage is similar for the three silver halides. Brice[48] finds the absorption of silver bromide and iodide vapors to be continuous below 3350A, with maxima about 3170A for both. The heat of dissociation for the normal states is 2.77 volts (silver bromide) and 3.02 volts (silver iodide), and for the excited states 0.21 and 0.10 volt, respectively. It could not be determined whether the products were metastable halogen and normal silver or metastable halogen and excited silver. Dutta[49] claims the normal form of silver halides in the vapor state to be ionic and not atomic.

Herzberg[50] has summarized the spectroscopic methods for determining the dissociation energies of diatomic molecules. These methods have been extended to polyatomic molecules. Mecke,[51] who discussed the mechanism of dissociation of molecules such as water, carbon dioxide, methane, formaldehyde and the nitrogen oxides, suggested that that atom is split off first which represents the smallest energy of dissociation.[52]

Terenin[53] observes that the photodecomposition of SnI_4 vapor by light of 2500-2150A is accompanied by a bright visible emission of the spectrum of the iodine molecule with an abnormal distribution of intensity in the bands. The iodine molecule is thought to be detached in one primary process. The whole process is equivalent to a recombination of the atoms in the act of photodissociation, or to a redistribution of the valency linkings. A marked temperature cofficient indicates the necessity for an energy of activation for this type of photodissociation. The mechanism of the yellow fluorescence in the vapor of bismuth iodide may be similarly explained; under the action of suitable quanta and with some thermal activation an iodine molecule may be detached from BiI_3.[54]

[47] Franck, J., and Kuhn, H., *Z. Physik,* **44,** 607 (1927).

[48] Brice, B. A., *Phys. Rev.,* **38,** 658 (1931).

[49] Dutta, A. K., *Trans. Bose Research Inst., Calcutta,* **8,** 248 (1932-3); *Chem. Abs.,* **29,** 6839 (1935).

[50] Herzberg, G., *Chem. Rev.,* **20,** 145 (1937).

[51] Mecke, R., *Z. physik. Chem.,* **7B,** 108 (1930).

[52] See also Kimura, M., *Sci. Papers Inst. Phys. Chem. Research, Tokyo,* **18,** 150 (1932).

[53] Terenin, A., *Nature,* **135,** 543 (1935); *Compt. rend. Acad. Sci. U.R.S.S.,* **1,** 482 (1934); **3,** 181 (1935); *Brit. Chem. Abs.* **A,** 807 (1935); Terenin, A., and Tshubarov, R., *Acta Physicochim. U.R.S.S.,* **7,** 1 (1937); *Chem. Abs.,* **32,** 3266 (1938); Parti, Y. P., and Samuel, R., *Proc. Roy. Soc.,* **49,** 568 (1937); see also Herzberg, G., and Teller, E., *Z. physik. Chem.,* **21B,** 410 (1933)] and van Manen, B., *Chem. Weekblad,* **34,** 549 (1937)] for polyatomic molecules.

[54] See also Neuïmin, H., *Physik. Z. Sowjetunion,* **2,** 422 (1932). For zinc and cadmium halides, see Deb, S., *Trans. Bose Research Institute, Calcutta,* **10,** 223 (1934-5); *Chem. Abs.,* **32,** 3263 (1938).

In the Schumann region, many molecules of inorganic or simple organic compounds become fluorescent because of dissociation into radicals, some of which are excited.[55] It is, however, unnecessary to discuss in detail the many contributions of spectroscopy to the heats of dissociation of inorganic compounds. The most accurate recent values for the heats of dissociation of various compounds as obtained by all available methods have been compared and tabulated by Rossini and Bichowsky.[56] The band spectra of many compounds will be discussed briefly in the consideration of individual photochemical reactions in the remaining chapters.

Predissociation Spectra

One feature of the band spectra of certain compounds requires special mention. Franck[57] as early as 1925 mentioned band spectra in which the rotational structure, sharp within the bands at longer wave-lengths, becomes diffuse at shorter ones. He gave the interpretation, no longer regarded as correct, that the rotational energy in such cases is actually great enough to dissociate the molecule. Such spectra had been described by Henri and Teves[58] who called them predissociation spectra. By 1929 this type of absorption had been observed in the spectra of more than 40 polyatomic molecules, such as sulfur dioxide, ammonia, nitrogen peroxide, etc. It is not, however, confined to polyatomic molecules, being exhibited by some diatomic molecules. Indeed, it was first discovered in the case of sulfur vapor in the bands of which the rotation lines disappear at 2792A, although the

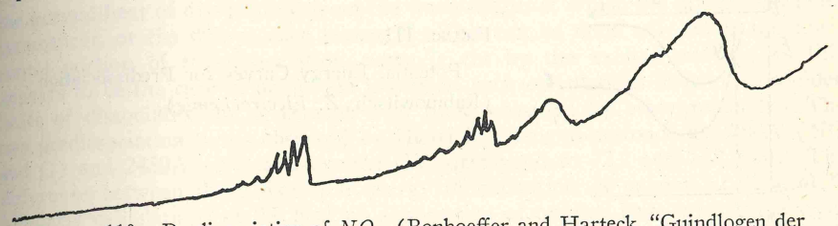


Figure 110. Predissociation of NO_2. (Bonhoeffer and Harteck, "Guindlogen der Photochemie," Courtesy, Th. Steinkoff, Dresden).

vibrational bands continue to shorter wave-lengths. Figure 110, showing the absorption of nitrogen peroxide, illustrates the phenomenon. In the bands at 2491 and 2459A, the quantized rotation lines are clearly evident, but they have disappeared in the vibration bands at 2447 and 2425A. In some, but not all, cases the region of predissociation is followed on the short-wave side by a region of continuous absorption. In other cases, the diffuse bands are found on both the long- and short-wave sides of bands with definite rotation lines so that a molecule may exhibit more than one region of predissociation.

Henri suggested the name predissociation because he believed that absorption in this region produced a new state of the molecule in which the latter is chemically active, labile, non-fluorescing and predisposed to dissociate. More recent studies have somewhat altered this concept. The interpretation of the phenomenon by the aid of potential energy curves and by the aid of an analogy with the Auger

[55] Neuïmin, H., and Terenin, A., *Bull. Acad. Sci. U.R.S.S., Classe sci. math. nat., Ser., phys.,* 529, 1936; *Chem. Abs.,* **31,** 3790 (1937).

[56] Rossini, F. D., and Bichowsky, F. R., "Thermochemistry of Chemical Substances," New York, Reinhold Publishing Corp., 1936.

[57] Franck, J., *Z. Elektrochem.,* **31,** 350 (1925).

[58] Henri, V., and Teves, M. P., *Nature,* **114,** 894 (1924); *Compt. rend.,* **179,** 1156 (1924).

effect in x-ray spectra [59] has been the subject of much work.[60] New criteria for the presence of this type of absorption have been given by Kaplan [61] who has investigated nitrogen spectra.[62]

In brief, it may be said that the phenomenon depends upon the existence of two excited states of the molecule the potential energy curves for which cross at a position which represents binding for one state and dissociation for the other. In Figure 111, the ground states are not represented for the molecules considered. In each case transitions from the ground state to excited state A are permitted but those to excited state C are forbidden. Assume that by the Franck-Condon principle the electron transition has raised the energy to the points marked X.[63] If only the state C existed, the molecule would suffer dissociation either immediately or after completing a half vibration. If, on the other hand, only the states A were possible, excited molecular states would result and these would account for the production of bands with rotational fine structure. After a brief life (10^{-8} second), they would emit part or all of their excitation energy as fluorescence. But when,

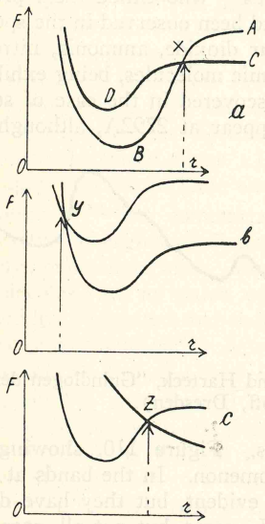


FIGURE 111.

Potential Energy Curves for Predissociation (Rabinowitsch, *Z. Electrochemie*).

as in the figure, two crossed excited states may exist, the molecule may vibrate along either curve. Thus a molecule if excited may during its life of 10^{-8} seconds perform many vibrations the period of which is of the order of only 10^{-13} second before it emits its energy as fluorescence. While it remains as a molecule, it is also rotating and a rotational line (or lines from different ones of the many molecules) is produced within the vibrational band. But during each time that, in the course of a vibration, it passes through the crossing point, the excited molecule stands a finite chance of changing by a "radiationless transition," which involves no change in potential energy, to curve C which leads to dissociation. Thus it is

[59] Bonhoeffer, K., and Farkas, L., *Z. physik. Chem.*, **134**, 337 (1927).

[60] Herzberg, G.: "Die Predissoziation und verwandte Erscheinungen," Springer, Berlin (1931); *Phys. Rev.*, **40**, 313 (1932).

[61] Kaplan, J., *Phys. Rev.*, **38**, 1079 (1931).

[62] Kaplan, J., *Phys. Rev.*, **41**, 114 (1932).

[63] Franck, J., and Sponer, H., *Nachr. Ges. Wissen. Göttingen*, 241 (1928).

that a single electronic transition gives (in the case of some of the molecules) rotational lines within a vibrational band while other molecules suffering the same electronic excitation undergo dissociation.

The width of each line of a spectrum is dependent upon the life of the excited state. In general, the longer the life, the narrower the line.[64] The net result of the dissociation of some of the molecules is to shorten the mean life of the excited molecules; the effect of this is to broaden the rotational lines of the absorption band. Because of this tendency the vibrational bands assume the diffuseness characteristic of predissociation. A second effect is a lessening of the intensity of the fluorescence. Fluorescence measurements offer an even more sensitive criterion for predissociation than does the effect of line-broadening although this test can only be used in gases at low pressures. Otherwise the fluorescence might be greatly affected by collisions.[65]

There are "selection rules" concerning the states which may exhibit predissociation,[66] but their consideration would lead us too far into specialized fields of molecular spectra. From a photochemical standpoint, in which we are primarily interested, the significance of the predissociation regions is that they represent regions of optical dissociation and as such are capable of yielding information in regard to the primary photochemical process in the reactions of the substances which exhibit such predissociation regions.

Since in the predissociation region the excitation energy must be at least equal to the dissociation energy, it is possible to calculate a maximum value for the normal heat of dissociation from the wave-length at which the diffuse spectrum commences, or the fluorescence lessens.[67] This can be done only when the horizontal portion of the dissociation curve is cut by the excited curve. As this appears to be the case in numerous instances, such calculations have often yielded heats of dissociation in agreement with those obtained by other methods. The two predissociation limits observed by Henri in nitrogen peroxide at 3700A (NO and O) and 2459A (NO and excited O) correspond to 72.2 and 117 kcal. The difference between these fixes the energy of excitation of oxygen at 45 kcal.[68] Similarly calculations of the heat of dissociation of oxygen have been made from the predissociation spectrum of sulfur dioxide. From predissociation limits, Bates [69] has calculated the heats of dissociation of OH and NH to be 116.05 and 102.2 kcal. Urey and Johnston [70] find the predissociation limit of chlorine dioxide to indicate an energy of dissociation through one mode of vibration of the excited electronic state into a ClO molecule and an oxygen atom.

Predissociation may be induced in certain cases in spectral regions normally showing discrete band spectra, by the addition of other gases. The change of absorption spectrum is practically independent of the nature of the foreign gas, at least in the case of the visible bromine spectrum observed by Avramenko and Kondrat'ev.[71] External magnetic fields may also cause induced predissociation.[72]

[64] The details of the theory of this relation must be sought in physical texts. The application of the Heisenberg uncertainty principle is involved. See also Rice, O. K., *Phys. Rev.*, **33**, 748 (1929); *J. Chem. Physics*, **1**, 375 (1933) and Kronig, R. de L., *Z. Physik*, **50**, 347 (1928).

[65] Kondrat'ev, V., and Polak, L., *Z. Physik*, **76**, 386 (1932).

[66] Kronig, R. de L., *Z. Physik*, **62**, 300 (1930).

[67] Turner, L. A., *Z. Physik*, **68**, 178 (1931).

[68] See also Herzberg, G., *Z. physik. Chem.*, **10B**, 189 (1930).

[69] Bates, J. R., *Z. physikal. Chem. Bodenstein Band*, 329 (1931).

[70] Urey, H. C., and Johnston, H., *Phys. Rev.*, **38**, 2131 (1931).

[71] Avramenko, L., and Kondrat'ev, V., *Physik. Z. Sowj.*, **10**, 741 (1936); *Chem. Abs.*, **31**, 8366 (1937). See also Loomis and Fuller, *Phys. Rev.*, **39**, 180 (1932); Kondrat'ev, V., and Polak, L., *Physik. Z. Sowj.*, **4**, 764 (1933).

[72] Turner, L., *Phys. Rev.*, **41**, 627 (1932).

A general discussion of induced predissociation and the predissociation of polyatomic molecules has been given by Burton and Rollefson.[73]

The principles followed in interpreting the predissociation spectra of diatomic molecules require amplification when applied to the spectra of polyatomic molecules so as to take into account the more complex nuclear vibrations and the fact that polyatomic products of decomposition contain vibrational and rotational energy, while for monatomic dissociation products only electron excitation energy need be considered. In the case of sulfur dioxide,[74] the energy value for the predissociation limit at 1950A is greater than the energy required for thermal dissociation into SO and O by about 13 kcal.; this must be divided between translational and vibrational and even some rotational energy.

A marked shifting of the region of predissociation to longer wave-lengths with increase in the temperature of the absorbing gas was noted by Henri in his work on predissociation. Joos and Hermann[75] have confirmed Herzberg's suggestion that this is due to the thermal excitation of higher vibrational levels in the ground electronic state, by observations on nitrogen peroxide at temperatures from $-15°$ to 500° These show that the sharpness of the individual bands is not affected by the rise in temperature. The temperature effect is of some significance for the temperature coefficients of certain photochemical changes.

Caution must be used in concluding that photochemical reactions brought about by light absorbed in a region of sharply banded absorption have an excited molecule mechanism,[76] since induced predissociation may occur in molecules showing any kind of light absorption. Furthermore, weak continuous absorption between the lines of a spectrum must not be neglected. Consideration of such absorption in the chlorine spectrum at wave-lengths longer than the convergence limit has led to a recent revision of the interpretation of the mechanism of the combination of hydrogen and chlorine induced by light in this region.[77]

Franck and Rabinowitsch[78] have stated that in the majority of photochemical reactions in gases every act of absorption leads to dissociation into atoms or free radicals, a point of view in which Lowry[79] concurs. West[80] tests for the paramagnetic free radicals by ability of the latter to effect the ortho-para hydrogen conversion. He applied the method with success to the detection of methyl radicals produced by the irradiation of methyl iodide and of acetone vapors. However, benzene and propionaldehyde when illuminated did not cause the ortho-para hydrogen conversion. Neuĭmin[81] uses a layer of molybdenum trioxide in the detection of atomic hydrogen, which forms an intense blue color, "molybdenum indigo."

[73] Burton, M., and Rollefson, G. K., *J. Chem. Phys.*, **6**, 416 (1938). For the case of sulfur, see Olsson, E., *Naturwiss.*, **25**, 781 (1937) and Lochte-Holtgreven, W., *Z. Physik*, **109**, 147, 149 (1938).

[74] Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932). For a general theoretical discussion of the predissociation of polyatomic molecules, see Dushinskiĭ, F., *Acta Physicochim. U.R.S.S.*, **5**, 651 (1936).

[75] Joos, G., and Hermann, A., *Physik. Z.*, **33**, 213 (1932).

[76] Rollefson, G. K., *J. Phys. Chem.*, **42**, 737 (1938).

[77] Bayliss, N. S., *Trans. Faraday Soc.*, **33**, 1339 (1937).

[78] Franck, J., and Rabinowitsch, E., *Trans. Faraday Soc.*, **30**, 120 (1934).

[79] Lowry, T. M., *Trans. Faraday Soc.*, **30**, 3 (1934).

[80] West, W., *J. Am. Chem. Soc.*, **57**, 1931 (1935).

[81] Neuĭmin, H., *Compt. rend. acad. sci., U.R.S.S.*, **16**, 447 (1937); *Chem. Abs.*, **32**, 1580 (1938).

Chapter 15

Overall Photochemical Reactions

It has been shown in the preceding chapters that it is advantageous to consider separately the mechanisms of the primary and secondary processes of photochemical reactions. Experimentally, however, there is no such demarcation and both must be studied simultaneously.

It is now generally recognized that for chemical reactions to proceed the molecules must be supplied with at least a minimal amount of energy known as the activation energy. This is usually not identical with the observed heat of reaction, the latter being merely the difference between the activation energies for the forward and reverse reactions. In purely thermal reactions, the activation energy is kinetic energy due to random collisions resulting from the heat motion of the molecules. Only those molecules which at the experimental temperature have energies in excess of the activation energy are capable of reacting. Since from the Maxwell-Boltzmann distribution law at ordinary temperatures only about one in 10^7 molecules of a gas possesses an energy equivalent to 25 kcal. per mole, reactions for which the activation energy is greater than this will be slow. The absorption of ultraviolet light may, however, readily supply the molecules with far greater amounts of energy so that the photochemical reaction may be rapid. Thus, the processes of dissociation or excitation attendant upon the absorption of light may yield atoms, free radicals or molecules with sufficient activation energy to allow the remaining secondary reactions to proceed readily.

Whether or not the secondary reactions do so depends upon the nature of the secondary reactions in which these primary products participate. If all the secondary reactions proceed at the experimental temperatures with negligible activation energies, or with activation energies compatible with those possessed by the primary products, the photochemical reaction will proceed. The rate of reaction is then determined by that of the primary process, which depends upon the rate of absorption of energy. If, on the other hand, the secondary processes require activation energies in excess of those possessed by the primary products the reaction will not proceed. In such cases, the temperature must be raised to one at which the requisite activation energy for the slowest necessary secondary process is available. The overall reaction will then have a temperature coefficient. In general, the primary process is not markedly dependent upon temperature, and purely photochemical reactions have temperature coefficients of unity. This means merely that none of the secondary processes requires activation energy. When there is a temperature coefficient, it is usually due, therefore, to one of the secondary processes requiring activation energy not sufficiently available at the usual experimental temperatures. Since most photoreactions occur through the intermediate formation of atoms and free radicals, an accurate knowledge of the rate constants of reactions in which these participate is of importance for the determination of the mechanisms of individual photoreactions.[1]

[1] Bates, J. R., *Chem. Rev.*, **17**, 401 (1935).

Photochemical Thresholds

Since it is the function of light in a photochemical reaction to supply the energy of activation for that reaction (or more strictly for its primary process), it should be necessary to employ a radiation of frequency corresponding to at least that energy. This implies the existence of a photochemical threshold frequency below which the reaction could not be brought about. Mecke[2] states that the accurate determination of this threshold wave-length is important for a proper understanding of the nature of the primary process, but notes that it unfortunately presents great experimental difficulties. Indeed, some workers have indicated these difficulties to be so great as to preclude experimental determination.

In the case of the combination of hydrogen and chlorine, Coehn and Jung[3] claimed to have found a threshold at 5400A, longer wave-lengths not leading to the formation of hydrogen chloride. On the other hand, Taylor[4] placed the threshold at 4900A. Both of these results were criticized by Bowen,[5] who showed that the results indicated no more than that the rate of reaction is proportional to the amount of light absorbed and that this drops to low values in these wave-length regions.

A similar attempt to find critical wave-lengths for the decomposition of ethyl and methyl iodides was due to Job and Emschwiller.[6] They considered the quantum at the critical wave-length for the decomposition (the "critical complement"), to measure the binding energy of the covalence C-I. By placing a tube of ethyl iodide in the spectrum of a carbon arc, it was noted that the reaction appeared to proceed as soon as wave-lengths shorter than 4100A were used. This corresponds (Figure 103) to 69.3 kcal. per mole. Methyl iodide gave this same value, but for iodobenzene it was 4000A or 71 kcal. However, Bowen[7] criticized these conclusions by showing that the threshold values were related either to the lower limits of the absorption spectrum or to the wave-length of maximum absorption. Bowen stated there was no theoretical justification for such conclusions. Warburg had attempted to relate thresholds to the heat of linking. The thermal values for the C-I linking gave only 40 kcal., whereas Job and Emschwiller had found 69.3 kcal. As has been indicated in an earlier chapter the heat of dissociation of such molecules as iodine into normal atoms is not related to the actual amounts of energy required to dissociate the molecule into a normal and an excited atom; this may be far greater. Therefore, heats of linking could not be calculated even from a knowledge of the convergence limit without a knowledge of the amount of excitation energy of the decomposition products. Allmand and Reeve[8] found the decomposition of oxalic and formic acids to proceed at a measurable rate in light of wave-lengths much longer than those computed by Volmar[9] from thermochemical data on the heats of unimolecular decomposition.

Schneider and Sperti[10] suggested the existence of threshold wave-lengths for

[2] Mecke, R., *Trans. Faraday Soc.*, **27**, 360 (1931).
[3] Coehn, A., and Jung, G., *Z. physik. Chem.*, **110**, 705 (1924).
[4] Taylor, W., *Phil. Mag.*, **49**, 1165 (1925).
[5] Bowen, E. J., *Phil. Mag.*, **50**, 879 (1925).
[6] Job, A., and Emschwiller, G., *Compt. rend.*, **179**, 52, 168 (1924).
[7] Bowen, E. J., *Trans. Faraday Soc.*, **21**, 543 (1926).
[8] Allmand, A. J., and Reeve, L., *J. Chem. Soc.*, **129**, 2852 (1926).
[9] Volmar, *Compt. rend.*, **178**, 697 (1924); **180**, 1172 (1925).
[10] Schneider, H., and Sperti, G., *Bull. Basic Sci. Research*, **1**, 7 (1926).

photochemical reactions. By means of a series of filters they found the longest wave-length capable of liberating iodine from a solution of potassium iodide to lie between 3340 and 3660A. Inasmuch as wave-bands covering as much as 320A units had to be used, it was not possible to determine whether or not the yield dropped suddenly to zero from fairly high values over a very narrow range of wave-lengths. These authors extended their point of view to the inactivation of the enzymes pepsin, rennet and invertase and to the killing of bacteria and protozoa as well.

Further tests of the question require accurate determinations of the quantum yields at a series of wave-lengths; a positive threshold would be indicated by a sudden drop to zero from a fairly high and constant quantum yield. Comparatively few such data are available, but those papers in which data adequate to the test have been given, *e.g.*, the work of Norrish[11] on the decomposition of nitrogen dioxide, indicate a sloping curve over a fairly wide range of wave-lengths. For this reaction the quantum yield is zero at 4360A, 0.72-0.74 at 4050A, 1.54-2.10 at 3650A and 2.07 at 3100-2700A. A possible explanation of the lack of sharpness in the change in quantum yield with wave-length may be that not all of the molecules of the absorbing material are initially in the same vibrational state. Those few molecules which at the temperature of the experiment may be in excited states may be expected to be activated by the absorption of smaller quanta than are required to activate those initially in lower vibrational states.[12] The heat of dissociation obtained spectroscopically by the absorption of a gas at a temperature other than absolute zero is the weighted mean of the heats of dissociation of the various vibrational excited states existing at the temperature at which the absorption occurs. Conversely, since these states have different heats of dissociation, the wave-length threshold for each should be definite, but for the mixture there should only be a sloping curve or a diffuse threshold.

By extrapolating the quantum yields of each of four reactions to a zero quantum yield, Rao and Dhar[13] found extrapolated threshold wave-lengths. The corresponding energies in kcals. per mole were found to agree closely with the energy of activation of the dark reactions. There was, however, in some of these a rather extended and uncertain extrapolation. Bowen had found much earlier that the activation energies of four bimolecular reactions calculated from their temperature coefficients could not be related to the energies corresponding to the long-wave limits of the absorption bands. Neither the absorption limit nor the activation energy bore any definite relation to the heats of linking of the bonds assumed to be ruptured in the photochemical processes.

Franck and Herzfeld[14] have emphasized the possibility, at least for polyatomic molecules, that thermal energy can contribute much more of the energy required for a photochemical change than had previously been assumed. Also, in such complicated molecules more than one absorbing center may be present. Energy absorbed by one linking may be transferred to another, which itself absorbs, so that the sum or a portion of the sum of the energies absorbed in separate portions of the molecule may be made available to affect a disruption of one or the other linking, the energy absorbed by that linking alone being insufficient for this purpose. The possibility of such intramolecular migrations of energy seems to

[11] Norrish, R. G. W., *J. Chem. Soc.*, 1604 (1929).
[12] Tolman, R. C., *J. Am. Chem. Soc.*, **42**, 2506 (1920); **45**, 2285 (1923).
[13] Rao, G. G., and Dhar, N. R., *J. Phys. Chem.*, **36**, 646 (1932).
[14] Franck, J., and Herzfeld, K. F., *J. Phys. Chem.*, **41**, 97 (1937).

have been definitely shown in the work of Norrish on the photochemistry of the aldehydes. (Chapter 22.)

Over wide ranges of wave-lengths there may be variations in the quantum yield with the wave-length. In many reactions, the quantum yield increases with the frequency. In the case of the hydrolysis of tetrachlorplatinic acid[15] the yield continues to increase over a range of 3080A, which coresponds to a range of energy levels far too great to be accounted for on the basis of a temperature distribution of vibrational states. The reasons for this phenomenon are not yet clear. Such results appear to be obtained chiefly in reactions involving polyatomic molecules in solution.

Temperature Coefficients

Since the secondary processes are thermal reactions, they may be expected to possess temperature coefficients different from unity. Nevertheless, early observations by Eder (1879) and by Goldberg[16] indicated most of the then known photochemical reactions to have temperature coefficients close to unity. Bancroft and Allen[17] disagreed and several reactions with higher values were brought forward by Plotnikow,[18] who proposed to classify photochemical reactions into three groups with temperature coefficients of 1.04, 1.20 and 1.45, respectively. Most reactions were thought to belong to the first group. The second group contained a few reactions in which it was suggested that diffusion processes determined the rate.[19] The third group comprised chiefly those reactions in which halogens were the absorbers. In determining the temperature coefficient, the effects of a possible dark reaction had to be eliminated either by working at very low temperatures and with light of high intensity or by subtracting dark rates determined in separate experiments. This latter step assumed the principle of the additivity of the rates of light and dark reactions, a principle for which there is little present justification.

The data at present available for a large number of reactions[20] show the distribution of temperature coefficients to be random, so that the Plotnikow classification into three groups has lost significance. Furthermore, the idea that the halogens fall into a special class was disproved by Hertel,[21] who found that the temperature coefficient for the hydrogen-chlorine combination has different values when light of different wave-length regions is employed. With light in the region of the band spectrum of chlorine, the temperature coefficient is 1.48, but with light within the continuous region at shorter wave-lengths, it is 1.37. In the presence of traces of oxygen, the true values may be masked, since 1.12 was stated to be the temperature coefficient of the reaction under such conditions.

It was early recognized that the temperature coefficient for a dark reaction should be expected to be higher than for a light reaction.[22] An indication of the

[15] Cited by Style, D. W. G., "Photochemistry," p. 69, Methuen, 1930, from Boll, M., *Ann. Physique*, **25**, 243 (1914).

[16] Goldberg, E., *Z. physik. Chem.*, **41**, 1 (1903); *Z. wiss. Phot.*, **4**, 56 (1906).

[17] Bancroft, W. D., and Allen, R. P., *Proc. Nat. Acad. Sci.*, **15**, 445 (1929).

[18] Plotnikow, J., *Z. physik. Chem.*, **78**, 573 (1911).

[19] See for certain reactions in liquid systems, Berthoud, A., and Bellenot, H., *J. chim. Phys.*, **21**, 308 (1924). Abel, E., and Schmid, H., *Monatsh.*, **61**, 361 (1932), find the temperature coefficient of a streaming reaction smaller than that of a quiet one.

[20] For tabulations of temperature coefficients, see Plotnikow, J., "Allgemeine Photochemie," 2nd Ed., de Gruyter, Berlin, 1936. Kistiakowsky, G. B., "Photochemical Processes," New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1928.

[21] Hertel, E., *Z. physik. Chem.*, **15B**, 325 (1932).

[22] Bodenstein, M., *Z. physik. Chem.*, **85**, 380 (1913).

[23] Banerji, R. C., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **134**, 172 (1924); *Chem. Abs.*, **18**, 2634 (1924).

relative magnitudes of the light and dark temperature coefficients for a number of reactions was given by Banerji and Dhar.[23] The decomposition of trichloracetic acid has a temperature coefficient of 3.0 in the light and of 4.28 in the dark. For the inversion of cane sugar they give the values 3.4 and 3.82, for the oxidation of sodium nitrite by iodine, 1.4 and 2.5, and for the action between oxalic and hydriodic acids 2.2-2.5 and 2.98 respectively.

Indian workers have devoted considerable attention to such determinations.[24] In general, it has been found that the temperature coefficients of light reactions vary with the wave-length of the incident light, although the coefficients are usually less than those of the corresponding thermal reactions. The greater the extent to which a reaction is accelerated by light, the smaller is the value of the temperature coefficient. Yajnik and Uppal were unable to find any relation between the temperature coefficients and the dielectric constants of the solvents employed.

Temperature coefficients less than unity are very rarely encountered. They could be interpreted as meaning that the temperature coefficient of some dark inhibiting reaction in a chain mechanism is greater than that of the chain-lengthening processes.

The temperature coefficients discussed in the preceding paragraphs are those of the velocities of reactions, the light intensity being held constant. The results recounted have held little general significance. More important theoretically are the results obtained when the amount of absorbed energy is maintained constant and the coefficients are computed for the quantum yields. Such values will differ from those of velocity measurements at constant incident intensity when the measurements are not made under conditions of total absorption if there is a dependence of the extinction coefficient upon the temperature.

In some cases a complex formed in a solution absorbs some of the light, as for example, the triiodide ion in reactions involving oxidation by iodine. In such a case, the light is partly absorbed by iodine and partly by the triiodide ion, only the former being effective. The amount of triiodide ion present depends upon the temperature since the reaction for its formation has a temperature coefficient. Accordingly, the photochemical reaction will have a temperature coefficient for its quantum yield dependent upon a temperature coefficient of the efficient absorption. Such reasoning may conceivably apply also to cases in which solvation of the absorbing molecule plays a prominent part.

But there is a more fundamental sense in which the process of absorption may be attended by temperature effects—there may be a variation of the extinction coefficient of a substance with temperature. Tolman[25] noted the possibility that a molecule might have to be raised to an energy state higher than that of the normal state before it would be capable of absorbing certain radiations. Otherwise stated, the probability of absorption might depend upon the original quantum state of the molecule. There is evidence that the absorption coefficients of gases possess temperature coefficients. v. Wartenberg[26] concluded that the absorption of longer wave-lengths by oxygen at 1800°C. gave evidence of being largely due to molecules possessing a considerable amount of internal energy.[27] However,

[24] Mukerji, B., and Dhar, N. R., *J. Phys. Chem.*, **33**, 850 (1929); Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Chem. Abs.*, **24**, 1035 (1930).

[25] Tolman, R. C., *J. Am. Chem. Soc.*, **42**, 2506 (1920); **45**, 2285 (1923).

[26] v. Wartenberg, H., *Physik. Z.*, **11**, 1168 (1910).

[27] See also observations on bromine by Ribaud, G., *Ann. Physique*, **12**, 107 (1919), and on chlorine by Dobbie, J. J., and Fox, J. J., *Proc. Roy. Soc.*, **99A**, 456 (1921) and by Kuhn, H., *Z. Physik*, **39**, 77 (1926).

the effects of temperature on light absorption are generally insufficient to account for the temperature coefficients of photochemical overall reactions. Since electronically excited states cannot be excited by thermal means, at least within the temperature ranges usually under consideration, the possibility of getting excited states is limited to that of vibrational states. However, for most gases, the number of molecules in any but the lowest few vibrational levels can usually be neglected. For this reason, the possibility raised by Tolman apparently is not of great practical significance. Young and Style [28] have given a detailed discussion of the manner in which a study of the temperature coefficient of a reaction may give information as to its mechanism. According to Dhar and Bhattacharya,[29] an increase in the absorption of light by a molecule is associated with increased chemical reactivity and a weakening of the binding forces. When a molecule becomes more reactive because of an increase in temperature or the presence of sensitizers it is likely to absorb light more markedly. It has been reported by Dhar and Bhargava,[30] that in certain cases, the light absorption of a mixture of substances may be greater than the sum of the absorptions of the separate substances. The increased absorption is attributed to an activation of molecules by the presence of other molecules. Fast reactions are claimed to show greater light absorption than do slower ones.

It is possible to eliminate the question of temperature effects on absorption when variations in the temperature coefficients do not occur in systems having a wide range of variation of the original concentration of the absorbing component. When effects due to a variation of the primary process with temperature can be eliminated, as is most generally the case, the temperature coefficients of the quantum yields of photochemical reactions give information regarding the mechanism of the secondary processes.[31] As such, they can best be discussed in connection with the individual reactions in which they are encountered. In general, it has been recognized that the temperature coefficients decrease as shorter wave-lengths of light are employed.[32] The use of shorter wave-length light usually gives an increased quantum yield but a smaller temperature coefficient, but exceptions are known.

Most of the sources of a temperature effect of a quantum yield—diffusion, change in viscosity of a solvent, thermal activation of some one of the secondary reactions—would tend to produce definite values of some energy of activation at the temperature of measurements, or else would cause the calculated thermal activation energy for an intermediary process to decrease when determined at higher temperatures. Nevertheless, Kistiakowsky [33] has found in two reactions—the oxidation of hydrogen and that of carbon monoxide, irradiated by an aluminum spark—temperature coefficients which increased with temperature. Style [34] makes the suggestion that in such cases collisions of the products of some highly exothermic secondary reaction with the absorbing molecules may activate the latter, some thermal activation energy being required for this process.

[28] Young, K. W., and Style, D. W. G., *Trans. Faraday Soc.*, **27**, 493 (1931).

[29] Dhar, N. R., and Bhattacharya, A. K., *Z. anorg. Chem.*, **176**, 372 (1928); *J. Indian Chem. Soc.*, **11**, 33, 311 (1934); *Chem. Abs.*, **28**, 3663, 6636 (1934).

[30] Dhar, N. R., and Bhargava, P. N., *Nature*, **134**, 848 (1934).

[31] Young, K. W., and Style, D. W. G., *loc. cit.*

[32] Padoa, M., *Atti accad. Lincei*, **25** (II), 168, 215 (1916); **24** (II), 97, 828 (1915); *Gazz. chim. ital.*, **55**, 87 (1925).

[33] Kistiakowsky, G. B., *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

[34] Style, D. W. G., "Photochemistry," Methuen, 75, 1930.

Kinetics of Photochemical Reactions

Many attempts to generalize regarding the rates of photochemical reactions have been made, but these have not proved very profitable because of the great complexity of the individual processes encountered. Conditions affecting the rate of absorption of light introduce many variables not encountered in the study of the kinetics of thermal reactions. The speed of stirring may influence the rate when most of the light is absorbed close to the window through which it enters. Photochemical processes may be aided by, opposed by, or independent of simultaneous thermal processes. The order of a given reaction conducted thermally may differ from that when it is conducted photochemically.

Bodenstein [35] believed the rate of absorption of light to be the principal factor controlling the velocity of photochemical reactions. The concentration of molecules other than the ones which absorb radiation was also recognized as an important factor. The simple law relating the rate of the reaction to the absorbed energy $dx/dt = KI_{abs.}$ is applicable only when the possibility of the transfer of the absorbed energy to other molecules by collisions is negligible.[36]

Wegscheider [37] developed a series of kinetic expressions based upon the conception that the rate is proportional to the light absorbed in a localized volume of the reaction mixture, rather than to the amount absorbed within the total volume. He extended his mathematical treatment [38] to the velocities of reactions with intermediary formation of excited molecules. Wegscheider believed the intensity of the light to enter the equation for the rate of formation of a product not as the first power, but as a power which gradually decreases to zero as the intensity decreases. The total absorption from the start of the reaction to the exhaustion of the absorbing component might, however, be independent of the intensity. He emphasized the possibility that the quantum yield might vary considerably during the course of a reaction, so that values determined over only a selected time interval might be more or less fortuitous. He noted also that only in cases in which the fate of the excited molecule follows a unimolecular law and the primary process is irreversible should it be expected that the quantum yield would be one. Recently, Wegscheider [39] has treated several systems by taking into account the light absorbed by the solvent and the reaction products as well as by the reacting substances. It is obvious that the secondary processes may be so complex in the individual case and so varied from reaction to reaction that attempts at generalizations in regard to the kinetics of overall reactions are not likely to be successful.

Several workers have attempted to classify reactions into those which are proportional to the first power of the light intensity and into those proportional to the square root of the intensity. From studies of nine inorganic reactions, Bhattacharya and Dhar [40] found two (those between chromic and oxalic acids and between potassium persulfate and potassium iodide) in accord with the first power law. The others were proportional to the square root of the intensity. They believed the latter to be the case for reactions with atomic oxygen as an inter-

[35] Bodenstein, M., *Trans. Faraday Soc.*, **21**, 525 (1926).

[36] For the dependence of the velocity of a photochemical reaction on the intensity of illumination, see also Gaviola, E., *Anales assoc. quim. Argentina*, **18**, 133 (1930).

[37] Wegscheider, R., *Rec. trav. chim.*, **44**, 1118 (1925); *Z. physik. Chem.*, **103**, 273 (1922).

[38] Wegscheider, R., *Monatsh.*, **51**, 285 (1929).

[39] Wegscheider, R., *Monatsh.*, **62**, 101 (1933).

[40] Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. Chem.*, **175**, 357 (1928); *J. Indian Chem. Soc.*, **6**, 473 (1929).

mediate. They stated that if the reactants exhibit marked absorption of light, the velocity of the reaction increases in proportion to, or more rapidly than in direct proportion to, an increase in the intensity of the light. For systems with but slight absorption of light, they considered the square root law to be valid. It was found possible in many cases to alter the rate of the dark reaction by the addition of accelerators or inhibitors. By increasing the dark rate and exposing the system to radiation which could be only slightly absorbed, a true photochemical reaction proportional to the square root of the intensity of the incident radiation or to the amount of energy absorbed, could be made to become proportional to the first power of the intensity. On the other hand, a reaction proportional to the incident intensity or to its square could be made proportional to the square root of the intensity by decreasing the velocity of the dark reaction and so increasing the photochemical velocity. These observations were extended by Mukerji and Dhar to include[41] some fifteen pairs of substances. In a few reactions (sodium formate and iodine, Rochelle salt and bromine, the oxidation of quinine sulfate by chromic acid) the rate was proportional to the square of the intensity. No relation was found between the velocity of reaction of oxalic acid with potassium permanganate and the intensity of the incident light. The other reactions studied fell into the two classes described by Bhattacharya and Dhar, who believe all true photochemical reactions (with negligible dark reactions) tend to be proportional to the half or lower power of the intensity of the incident radiation.

Cases in which the rate appears to increase more rapidly than the intensity of the light are attributed by Bhagwat[42] to the presence of inhibitors which are relatively less effective in retarding the reaction when the intensity of the light is high. Bhagwat and Dhar[43] also assert that when the reaction velocity is not directly proportional to the light absorption, stirring will tend to increase the rate and decrease the temperature coefficient. However, when the velocity is directly proportional to the absorption, stirring will have no effect on the velocity of the reaction or the temperature coefficient.

Allmand[44] found that if the product of the extinction coefficient and the thickness of the absorbing layer is very small, the quantum efficiency for any wavelength is inversely proportional to the square root of the rate of energy absorption. If the thickness of the absorbing layer is continuously increased from a very small value until it becomes great enough to make the absorption of the incident energy complete, the limiting value of the quantum efficiency is twice as great as that in thin layers.

Recent work on chain reactions has indicated that in general the square root relation may be expected if the substance which acts as intermediary in carrying the chain is formed at a rate proportional to the intensity, but does not hold when the intermediary substance is formed at a rate proportional to the square of its concentration.[45] Since in many reactions the chains are carried by atoms liberated in the primary process and since these atoms are removed by three-body collisions involving two atoms, the first-mentioned conditions are frequently met. This accounts for the number of reactions for which the square root law has been found to hold with a fair degree of approximation. Bhagwat[46] believes the square

[41] Mukerji, B. K., and Dhar, N. R., *J. Phys. Chem.*, **32**, 1308 (1928).

[42] Bhagwat, W. V., *J. Indian Chem. Soc.*, **11**, 443 (1934); *Chem. Abs.*, **28**, 7163 (1934).

[43] Bhagwat, W. V., and Dhar, N. R., *J. Indian Chem. Soc.*, **9**, 335 (1932); *Chem. Abs.*, **27**, 27 (1933).

[44] Allmand, A. J., *J. Chem. Soc.*, 1557 (1929).

[45] Style, D. W. G., "Photochemistry," p. 51, Methuen, London, 1930.

[46] Bhagwat, W. V., *J. Indian Chem. Soc.*, **11**, 443 (1934); *Chem. Abs.*, **28**, 7163 (1934).

root relationship is more likely to be observed in the region of high frequencies than in that of lower ones.

Attempts to relate the rates of photochemical reactions to the dielectric constants of the solvents employed have not proved very profitable. Winther[47] found that, in the photoöxidation of iodoform and the polymerization of anthracene in a series of solvents, the velocity in general decreased with increasing dielectric constant of the solvent, but this could not be confirmed by Yajnik and Uppal.[48]

The earlier investigations are replete with instances of photochemical induction periods, or lags between the beginning of irradiation and start of reaction, and also of after-effects or a continuation of reaction after the close of the irradiation period. These effects are no longer regarded as of great general significance, the many known examples being considered merely as features of the mechanisms of the specific reactions in which they are encountered. At present, induction periods are usually regarded as the times required for the photochemical destruction of certain inhibitors present in small quantities.[49] Reactions claimed to exhibit after-effects have been reported by Mukerji and Dhar.[50] It must be noted that in chain reactions the reaction does not cease instantly when the illumination is cut off, as the secondary reactions continue for some time until all chains are broken. Similarly, when the intermediary in the chains is being formed and a stationary concentration (at which formation and destruction of the intermediary are equal) is being built up, the rate of the overall reaction (which depends upon the rate of destruction) need not attain its full value.

The influence of surface catalysts is of importance chiefly as they influence the recombination rate of free atoms or radicals. Coehn and Heymer[51] devised experiments in which hydrogen and chlorine were exposed to light without an opportunity of coming into contact with a solid surface. The formation of hydrogen chloride under these conditions proves that the reaction does not depend on an initial catalysis at a glass wall. Chapman and Grigg[52] have found the rate of this reaction to be less in capillary tubes than in wider ones. This is interpreted as meaning that the reaction is carried out (see Chapter 18) by means of an unstable catalyst (hydrogen and chlorine atoms) the latter being formed by light; these atoms are destroyed by recombination when they come in contact with glass.

Although irradiation of a graphite catalyst almost triples the rate at which it decomposes hydrogen peroxide, the effect is smaller for irradiated lead peroxide and still smaller or even non-existent in the case of smooth or slightly platinized platinum.[53] In the case of the decomposition at the surface of colloidal platinum,

[47] Winther, C., *Trans. Faraday Soc.*, **21**, 595 (1926); see also Mathur, K. G., Gupta, R. S., and Bhatnagar, S. S., *Indian J. Physics*, **2**, 243 (1927).

[48] Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Brit. Chem. Abs.* **A**, 174 (1930); *Chem. Abs.*, **24**, 1035 (1930).

[49] Earlier points of view are given by Purkayastha, R. M., *J. Indian Chem. Soc.*, **5**, 721 (1928); *Chem. Abs.*, **23**, 2105 (1929).

[50] Mukerji, B. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **2**, 277 (1925); **5**, 203 (1928); *Chem. Abs.*, **23**, 41 (1929); *Quart. J. Indian Chem. Soc.*, **2**, 277 (1925); *Chem. Abs.*, **20**, 1953 (1926).

[51] Coehn, A., and Heymer, G., *Ber.*, **59B**, 1794 (1926).

[52] Chapman, D. L., and Grigg, P. P., *J. Chem. Soc.*, 3233 (1928).

[53] Pisarzhevskii, L. V., Korabel'nik, R. K., and Ruinskaya, E. S., *Bull. acad. sci. U.R.S.S., Classe sci. math. nat.*, 931 (1934); *Chem. Abs.*, **29**, 2433 (1935).

the velocity constant is the sum of those of the action of ultraviolet light and of the colloid separately on hydrogen peroxide.[54]

Photochemical Effects of Intermittent and Polychromatic Light

The possibility of producing different effects by irradiating a system with a given quantity of intermittent or continuous light has been studied, notably by Padoa and Vita.[55] In some reactions, they claimed to secure greater reaction velocities by the use of intermittent light. The light was obtained by employing rotating sectors with a continuous source. In some instances the yield at first increased with the number of alternations of the sectors and then decreased to a constant value.[56]

Alternations of two or more colors with no periods of darkness caused a greater dependence of the yield on the velocity of alternation. Pulsating monochromatic light was also employed in some of their work.[57] The augmentation in yield depended both upon the wave-length of the light and the frequency of interruption, the maximum interruption being 560 times per second. In the oxidation of ferrous iodide by the 4607A line, the velocity was doubled by the use of intermittent light. This maximum rate was said to occur periodically as the frequency of interruption was increased, the maxima appearing irregularly at interruption frequencies of 32, 98, 138, 157, 202, 253, 270, 318, 357, 390, 450 and 513 per second. With green light, the yield ratio was lower (1.70), and the maxima fewer in number, occurring at 22, 259 and 532 interruptions per second. With yellow light the maximum ratio was 1.62 at 311 interruptions per second. Except at frequencies between 20, 40 and 260-370 interruptions per second, the yield was unaltered by intermittent illumination with this light. Red light gave a maximum yield ratio of 1.37 at 472 interruptions per second. The authors suggested that the periodic maxima might be due to the formation of active molecules which are the seats of adiabatic transformations, and that the life of these molecules is greater the greater their energy levels. Berthoud[58] was unable to confirm the existence of these maxima.

Berthoud and Bellenot[59] and Briers, Chapman and Walters[60] have used the rotating sector method in studying reactions whose rates are proportional to the square root of the light intensity, *e.g.*, the oxidation of potassium oxalate by iodine. The rate of the reaction varies as the concentration (in a steady state) of an intermediary, here assumed to be iodine atoms. The latter were formed at a rate proportional to the intensity of the light and destroyed at a rate proportional to the square of the concentration of the intermediary. The concentration of the catalyst in the steady state can therefore be shown to be proportional to the square root of the light intensity. When the sector rotates so rapidly that the secondary processes continue throughout the interval of darkness the rate is independent of the speed of rotation. When it rotates so slowly that the intermediary is exhausted by the secondary processes during each period of darkness, or is materially lowered in

[54] Suirkin, Y., and Godnev, I. N., *J. Phys. Chem. (U.S.S.R.)*, **5**, 32 (1934); *Chem. Abs.*, **28**, 4971 (1934). For other reactions in which surface effects have been held to play a part, see Kondrat'ev, V., *Z. Physik*, **48**, 310 (1928) and Kautsky, H., de Bruijn, H., Neuwirth, R., and Baumeister, W., *Ber.*, **66B**, 1588 (1933).

[55] Padoa, M., and Vita, N., *Gaz. chim. Ital.*, **57**, 187 (1927).

[56] Padoa, M., and Vita, N., *Atti II Congr. Naz. Chim. Pura Applica.*, 1256 (1926).

[57] Padoa, M., and Vita, N., *Gaz. chim. ital.*, **58**, 461 (1928).

[58] Berthoud, A., *J. chim. phys.*, **26**, 444 (1929).

[59] Berthoud, A., and Bellenot, H., *Helv. Chim. Acta*, **7**, 307 (1924).

[60] Briers, F., Chapman, D. L., and Walters, E., *J. Chem. Soc.*, 562 (1926).

[61] Briers, F., and Chapman, D. L., *J. Chem. Soc.*, 1802 (1928).

concentration during this period, the rate of the overall reaction will be lowered. By this method the life of the catalyst or intermediary has been calculated to be 0.03 to 0.12 second. Similar effects were observed by Briers and Chapman[61] in the case of the photosynthesis of hydrogen bromide, the mean life of the intermediary being 0.063 second.

Since truly monochromatic radiations are idealizations, all actual photochemical reactions are produced by the simultaneous action of more than one wave-length, even though these be but slightly different. Considerable work has been expended upon the effects produced by the simultaneous use of relatively widely separated wave-lengths. Plotnikow[62] claimed that the rate of bromination of cinnamic acid in carbon tetrachloride solution when simultaneously illuminated by several wave-lengths was less, in the ratio of 100 to 158, than the sum of the rates of the individual reactions when the wave-lengths were employed separately. Padoa and Vita[63] reported a confirmation of this behavior; they claimed also that the reaction rate does not decrease as the source is removed to greater distances to the extent demanded by the inverse square law. They reported a similar effect of complex light in diminishing the reaction rate of the decomposition of hydriodic acid, using 5460 and 5790A.[64] The opposite effect was reported in the case of the hydrogen-chlorine combination and in the action of light on direct-printing photographic paper, although in the latter case the order of the application of the wave-lengths used appeared to be a deciding factor.[65] Similar effects were also reported for the decomposition of ferric oxalate.

On the other hand, Berthoud,[66] who studied the oxidation of potassium nitrite by iodine in aqueous solution in yellow and blue light separately and together, found the effects to be purely additive. Winther[67] stated that the Italian workers neglected the induction periods of the reactions studied, employed incorrect methods of determining the rate of liberation of iodine in the hydrogen iodide decomposition, and employed erroneous transmission values for the filters.[68] It would appear that an interpretation of the Padoa experiments, assuming them to be correct, would imply that certain wave-lengths retard the effects produced by others. This raises the question as to whether any instances are known in which thermal reactions are retarded by light. Claims that such is the case were made by Chastaing[69] and by Trautz.[70] Details need not be given since re-examination of these reactions by Allmand and Maddison[71] failed to confirm the existence of the retarding effect; this has since been admitted by Trautz. With Haas, however, Trautz has recently[72] claimed that blue light accelerates and infrared retards the oxidation of benzaldehyde. It may be noted that it has frequently been suggested that the biological effects of ultraviolet rays may be annulled, at least in part by infrared rays.[73] However, others have proposed that the two forms of

[62] Plotnikow, J., *Z. physik. Chem.*, **79**, 641 (1912).

[63] Padoa, M., and Vita, N., *Gaz. chim. Ital.*, **56**, 375 (1926); *Trans. Faraday Soc.*, **21**, 573 (1926).

[64] See also *Z. wiss. Phot.*, **28**, 153 (1930); Vita, N., *Gazz. chim. Ital.*, **63**, 223 (1933).

[65] Padoa, M., and Vita, N., *Gaz. chim. Ital.*, **56**, 164 (1926); *Chem. Abs.*, **20**, 2951 (1926); *Gaz. chim. ital.*, **58**, 3 (1928).

[66] Berthoud, A., *J. chim. phys.*, **26**, 435 (1929).

[67] Winther, C., *Z. wiss. Phot.*, **31**, 251 (1933); **33**, 52 (1934).

[68] See also for further details of the controversy *Z. wiss. Phot.*, **32**, 185 (1933).

[69] Chastaing, P., *Ann. Chim. Phys.*, **11**, 145 (1877).

[70] Trautz, M., *Physik. Z.*, **7**, 899 (1906); *Z. Elektrochem.*, **13**, 550 (1907).

[71] Allmand, A. J., and Maddison, R. E. W., *J. Chem. Soc.*, 650 (1927).

[72] Trautz, M., and Haas, H. E., *Z. wiss. Phot.*, **33**, 81, 129 (1934); *Chem. Abs.*, **29**, 2869 (1935).

[73] Pech, J. L., *J. med. Bordeaux*, **10**, 434 (1925).

radiation should be applied simultaneously.[74] The Herschel effect in photography appears to be a case in which infrared radiations annul the effects of visible or ultraviolet radiations.

Plotnikow [75] has called attention to reactions which appear to proceed at periodic rates when illumination is furnished by complex light. He believes the concentration of free halogen in solutions of either bromine or chlorine in carbon tetrachloride to undergo periodic fluctuations when irradiated for prolonged periods with complex, but not with monochromatic, light.

[74] Rowley, C. D., and Larsky, A. W., British P. 325,824 (1928).
[75] Plotnikow, J., *Z. Physik*, **32**, 942 (1925).

Chapter 16

Photosensitized Processes

In photosensitized processes, the light which causes the reaction to proceed is absorbed, not by the reactants, but by some added substance which is capable of passing on the absorbed energy, or a sufficient portion of it, to the reactants. The simplest of such processes are those in which atoms act as photosensitizers.[1] Turner reviewed the earlier work on the excited systems formed when atoms absorb definite wave-lengths. Certain widely used terms regarding the nature of collisions in which excited atoms take part were introduced by Klein and Rosseland in 1921.[2] They called "collisions of the first kind" those in which a portion of the kinetic energy of two colliding atoms is expended in raising one of the atoms to an excited state. If, on the other hand, an excited atom loses a portion of its excitation energy during a collision, it is said to undergo a "collision of the second kind." It was demonstrated by Cario and Franck [3] that mercury atoms which had been excited by the absorption of radiations of the wave-length 2537A, a mercury resonance line, can undergo collisions of the second kind with thallium or sodium atoms. This means that during the collision the mercury atom passes some of its excitation energy to the atom with which it collides, raising the latter to an excited state. The excess of energy possessed by the excited mercury atom over that required to excite the thallium or sodium atom is converted into kinetic energy of the atoms separating after the collision. The excited alkali atom then, after a brief period, drops back to its normal state emitting the line corresponding to the energy lost in the transition from the excited state attained as the result of the collision. The effect observed experimentally is that, when a mixture of sodium and mercury vapors is irradiated with a monochromatic ray which is absorbed only by the mercury, the mixture emits a ray characteristic of sodium. Turner found that in processes of this kind, the excited mercury atom usually drops to the longer-lived metastable state before colliding with other atoms, at least under certain conditions of pressure.[4] Stuart's experiments [4a] on the quenching of the resonance fluorescence of mercury by radiationless collisions with foreign gas atoms indicated the excited mercury atom to have a larger effective radius that it has in the normal state.

The possibility that such collisions of the second kind of excited atoms with molecules might induce the molecules to enter reactions was soon recognized. Taylor, Marshall and Bates [5] found that hydrogen could be made to combine with oxygen when the gas mixture which had been bubbled through liquid mercury at the ordinary temperature, is irradiated with the resonance line of mercury

[1] Turner, L. A., *J. Phys. Chem.*, **32**, 507 (1928). For a detailed discussion, see Mitchell, A. C. G., and Zemansky, M. W., "Resonance Radiation and Excited Atoms," Cambridge Univ. Press, 1934.
[2] Klein, O., and Rosseland, S., *Z. Physik*, **4**, 46 (1921).
[3] Cario, G., *Z. Physik*, **10**, 185 (1922); Cario, G., and Franck, J., *Ibid.*, **11**, 161 (1922); **17**, 202 (1923).
[4] See also Donat, K., *Z. Physik*, **29**, 345 (1925); Wood, R. W., *Proc. Roy. Soc. London*, **106A**, 679 (1924).
[4a] Stuart, H. A., *Z. Physik*, **32**, 262 (1925).
[5] Taylor, H. S., Marshall, A. L., and Bates, J. R., *Nature*, **117**, 267 (1926); see also Senftleben, H., and Rehren, I., *Z. Physik*, **37**, 529 (1926) for the discussion of water vapor.

obtained by the use of a cooled mercury arc. Such a reaction could not be induced by this line in the absence of mercury vapor.[6] At high rates of gas flow, hydrogen peroxide could be detected as a product of the reaction, and some mercuric oxide formed on the surface of the metal.[7] Taylor [8] reviewed the early work on this and many other gas reactions and claimed to have reduced carbon monoxide to formaldehyde, methane and polymerized hydrocarbons by this method. Similar work was reported by Hirst.[9] Taylor, Marshall and Bates [10] showed that the function of the mercury surface was merely to furnish mercury atoms, the reaction occurring in the vapor phase. Mercury atoms adsorbed on a copper catalyst [11] are usually not activated sufficiently in the light of a mercury arc to cause a reaction between hydrogen and ethylene.

In the mercury-sensitized, hydrogen-ethylene reaction, there are formed ethane, methane, propane and butane.[12] Three primary reactions are postulated:

(1) $H_2 + Hg^* \longrightarrow Hg + 2H$.
(2) A splitting off of hydrogen from ethylene.
(3) The opening of the ethylene double bond.

The last reaction is possible since it requires less energy than that corresponding to the 4.9 volts or 112 kcal. of excitation energy of the mercury atom. Bates and Taylor [13] extended the method to a wide variety of reactions, including many organic compounds. They found the excited mercury atom highly efficient in breaking the linkings, H—H, N—H and O—H. The decompositions obtained were often many hundreds of times those obtained by exposure of the reactants to the complete ultraviolet spectrum of the mercury arc without the addition of the sensitizer. From this it followed that the energies of these bonds must all be less than 112 kcal., a conclusion substantiated by thermal data. In the breakdown of ammonia, the percentage of hydrogen in the reaction products was found to be be greatly in excess of that required had a simple decomposition to the elements occurred. It was therefore, suggested that the reaction occurs in stages, in such a way that some nitrogen-rich substance such as hydrazine can be formed.[14] Mitchell [15] also reported on the fluorescence of ammonia excited by collisions with excited mercury atoms. Bates and Taylor [16] extended the investigation to sensitizations by cadmium vapor, but Bates found that cadmium atoms excited to the 2^3P_1 state did not possess sufficient energy to effect the reaction between hydrogen and ethylene.[17] The possibility of such a reaction can at present be determined directly from the energy-level diagram of the atom proposed as sensitizer and from the thermally known energy requirement for the reaction in question. In general, it has been found to be true that collisions of the second kind are most probable when the

[6] Dickinson, R. G., *Proc. Nat. Acad. Sci.*, **10**, 409 (1924); Marshall, A. L., *J. Phys. Chem.*, **30**, 34, 1078 (1926).

[7] See also Bonhoeffer, K. F., and Loeb, S., *Z. physik. Chem.*, **119**, 474 (1926), and Hirst, H. S., and Rideal, E. K., *Nature*, **117**, 449 (1926).

[8] Taylor, H. S., *Trans. Faraday Soc.*, **21**, 560 (1926).

[9] Hirst, H. S., *Proc. Cambridge Phil. Soc.*, **23**, 162 (1926); *Chem. Abs.*, **20**, 2459 (1926).

[10] Taylor, H. S., Marshall, A. L., and Bates, J. R., *Nature*, **117**, 267 (1926).

[11] Ryerson, L. H., *Physics*, **2**, 70 (1932); for a recent summary, Norrish, R. G. W., *Trans. Faraday Soc.*, **35**, 21 (1939).

[12] Olson, A. R., and Meyers, C. H., *J. Am. Chem. Soc.*, **48**, 389 (1926); **49**, 3131 (1927).

[13] Bates, J. R., and Taylor, H. S., *Proc. Nat. Acad. Sci.*, **12**, 714 (1926); *J. Am. Chem. Soc.*, **49**, 2438 (1927).

[14] See also Dickinson, R. G., and Mitchell, A. C. G., *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

[15] Mitchell, A. G. G., *J. Am. Chem. Soc.*, **49**, 2699 (1927).

[16] Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, **50**, 771 (1928).

[17] Bates, J. R., *Proc. Nat. Acad. Sci.*, **14**, 849 (1928).

energy of the excited atom can be almost entirely consumed in the excitation of another atom or the disruption of a molecule. Processes in which there is much excess energy of excitation to be converted into kinetic energy are less probable.

Apparatus for effecting gas reactions photosensitized by metal vapors has been patented.[18] Among the reactions for which it was intended was the conversion of water gas into formaldehyde.[19]

It is a comparatively simple step from the consideration of these reactions to that of those in which the sensitizer is a molecule rather than an atom. Dhar and Mukerji [20] and also Berthoud [21] discussed the use of chlorine as a sensitizer for the decomposition of ozone, and Taylor and Emeléus [22] considered photosensitization by means of ammonia. In such cases, one is dealing with dissociated and not excited molecules. The dissociation products can initiate chain reactions. Details of these processes will be considered in later chapters in dealing with individual reactions.

Other Theories of Photosensitization.[23] Many instances of photosensitization by solids, as zinc oxide, have been described. Colloidal hydrous stannic oxide or ignited stannic oxide is said to enable sunlight to effect the oxidation of ammonia to nitrite or the reduction of nitrates to nitrites, and also to decolorize such dyes as methyl violet, methylene blue or brilliant green. The yields are very small.[24]

Irradiation of a crystal of cadmium sulfide so alters the potential of its surface field as to lessen its ability to adsorb phenolphthalein from an alcoholic solution.[25]

A novel theory of sensitized photolysis, developed by Baur [26] to explain the action of zinc oxide or uranyl salts in promoting various photochemical processes, has also been extended to cover certain cases of sensitization by dyes. The sensitizer is thought to become on absorption of light a polarized molecule, comparable to the two electrodes of an electrolytic cell.[27] In the case of uranyl salts, the absorption process is written:

$$5U^{VI} + h\nu \longrightarrow \begin{cases} 3U^{VIII} \\ 2U^{III} \end{cases}$$

In a more general form, it may be written:

$$U^{VI} + h\nu \longrightarrow U^{VI} \begin{cases} \oplus\oplus \\ \ominus\ominus \end{cases}$$

The displaced electrons return to their original state through a "molecular electrolysis," the energy for which is derived from the increase in the potential energy of the valence electrons attained during the process of light absorption. The

[18] I. G. Farbenindustrie A.-G., British P. 307,406, Feb. 11, 1927; 307,521, Feb. 11, 1927; *Chem. Abs.*, **23**, 5112 (1929).

[19] See also Frankenburger, W., and Steigerwald, C., German P. 513,461, Nov. 21, 1926; *Chem. Abs.*, **25**, 1303 (1931); Frankenburger, W., and Mayrhofer, K., German P. 528,040, Sept. 4, 1927 (to I. G. Farbenindustrie); Buttolph, L. J., U. S. P. 1,844,421, Feb. 9, 1932 (to General Electric Vapor Lamp Co.).

[20] Dhar, N. R., and Mukerji, B. K., *Trans. Faraday Soc.*, **21**, 645 (1926).

[21] Berthoud, A., *Trans. Faraday Soc.*, **21**, 554 (1926).

[22] Taylor, H. S., and Emeléus, H. J., *J. Am. Chem. Soc.*, **52**, 2150 (1930).

[23] Work on photosensitization has been reviewed by Farkas, L., Haber, F., and Harteck, P., *Z. Elektrochem.*, **36**, 711 (1930) and by Livingston, R., *J. Chem. Ed.*, **11**, 400 (1934).

[24] Varadanam, C. I., and Rao, G. G., *Current Sci.*, **7**, 231 (1938); *Chem. Abs.*, **33**, 1598 (1939).

[25] Hedvall, J. A., and Gohn, G., *Nature*, **143**, 330 (1939); note also Vartanyan, A. T., *J. Gen. Chem. (U.S.S.R.)*, **8**, 1098 (1938); *Chem. Abs.*, **33**, 4878 (1939).

[26] Baur, E., *Helv. Chim. Acta*, **1**, 186 (1918); **12**, 793 (1929); *Z. Elektrochem.*, **34**, 595 (1928).

[27] Burgher, K., *Z. wiss. Phot.*, **24**, 393 (1927). Baur has attempted to use his concept in explaining the assimilation of carbon dioxide by plants, *Helv. Chim. Acta*, **20**, 387 (1937).

positive and negative poles in the molecule act as anode and cathode in a kind of molecular electrolysis. Using silver nitrate as cathodic depolarizer and sucrose, glycine or glycerol as anodic depolarizer, the sensitizing action of the following dyes has been studied: rhodamine B, eosin, safranine-G, phenosafranine, fluorescein, methyl violet, chromotrope-2R. The photolysis results in the separation of silver and the concomitant formation of oxidation products. Some silver was liberated in the binary systems, silver nitrate-dye, silver nitrate-sucrose, but a larger amount was set free in the ternary systems composed of dye and depolarizers.

The sensitized photolysis very soon reaches a stationary state, apparently owing to the formation of a new anodic depolarizer which begins to compete with the existing depolarizer. The experiments with glycine and glycerol show that these substances can be further oxidized in this manner.

The investigation of Burgher lends support to an inner polarization mechanism for sensitization. It may also be noted that in certain instances photosensitization may be ascribed to the absorption of light by complexes formed between the sensitizer and one of the reactants, neither of the components absorbing alone. Instances will be discussed in the treatment of specific reactions.

The ability of a series of complex cobalt salts to sensitize the oxidation of potassium iodide, pyrogallol, benzidine, *p*-phenylenediamine and other substances when both the substrate and sensitizer are irradiated, usually by the 3660A line, was studied by Watanabe.[28] Of the nitro-cobaltic compounds, those which had two nitro-groups attached to the nucleus were most strongly affected by light. The oxidizing ability of the croceo-chloride (*trans*) was more photosensitive than that of the flavo-chloride (*cis*), which showed oxidizing action even in darkness. The magnitude of the photoactivity of nuclei of the type $Co(NH_3)_5X$ was influenced by the coordinated acid radical in the order $SCN > NO_2 > CO_3 > Cl$.

Mukerji and Dhar[29] find that in photosensitized systems there is a marked increase in the light absorption not found in systems they believe to be photo-inhibited. Dhar and Bhattacharya[30] suggest that the presence of a second reactant may sensitize molecules to radiation of longer wave-length.

Relation of Fluorescence to Sensitization.[31] An understanding of the nature of the photodynamic action of many fluorescent dyes upon living organisms (Chapter 42) and of the function of chlorophyll in the photosynthesis of carbohydrates (Chapter 43) depends upon the advances in our knowledge of the mechanism of photosensitization by these fluorescent substances. A much discussed recent question is whether the reactions effected by these agents are to be ascribed to their fluorescence or whether this property is merely an incidental phenomenon which may even lessen their effectiveness as sensitizers. Viale[32] believed that, since the additions of foreign substances to dyes lessened both their fluorescence and their effectiveness as sensitizers, the fluorescence was in some manner responsible for their sensitizing action. West, Müller and Jette,[33] however, pointed out that any addition of ions in solution which tends to destroy an activated molecule will simultaneously destroy the ability of that molecule to impart its energy to a chemical reaction or to emit it as fluorescence. The addition of reactants, which

[28] Watanabe, A., *Iwata Inst. Plant Biochem. Publ.*, **2**, 129 (1936); *Chem. Abs.*, **30**, 6650 (1936).

[29] Mukerji, B. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **5**, 411 (1928); *Chem. Abs.*, **23**, 40 (1929).

[30] Dhar, N. R., and Bhattacharya, A. K., *J. Indian Chem. Soc.*, **11**, 33 (1934); *Brit. Chem. Abs.*, 1934A, 496.

[31] For earlier theoretical discussions, see Steigmann, A., *Kolloid-Z.*, **44**, 173, 248 (1928); *Z. wiss. Phot.*, **26**, 299 (1929).

[32] Viale, G., *Arch. ital. biol.*, **73**, 19 (1924); *Chem. Abs.*, **19**, 2346 (1925).

[33] West, W., Müller, R. H., and Jette, E., *Proc. Roy. Soc. London*, **121A**, 294, 299, 313 (1928).

may remove excitation energy by collisions of the second kind and thus render it available to the reaction, also decreases the fluorescence. Many believe that the primary process in the reactions underlying photodynamic oxidations by dyes is the quenching of their fluorescence in solution by reactants.[34] Others, however, believe that, in general, photosensitized reactions in solution proceed rather by the use of energy absorbed in linkings or parts of the sensitizing molecule which never appears as fluorescence.[35]

The mechanism of the fluorescence of dyes and of its quenching has been the subject of much recent work. The advances in this, possibly the phase of photochemistry at present the most rapidly developing, have been summarized in a recent discussion of the Faraday Society.[36] Although the subject is still in a somewhat confused state, certain concepts have emerged.

Pringsheim[37] points out that fluorescence is the exception rather than the rule in organic molecules, most substances with large light absorption converting the energy thus acquired into heat by little understood mechanisms. He finds little known regarding the conditions that must be met in order that a substance in a condensed phase may fluoresce. One view is that, since the absorption of fluorescent dyes lies in the visible region, the quanta gained by absorption are too small to initiate quenching processes and, therefore, can only be lost by fluorescence. This seems inadequate since a large number of dyes with visible absorption are not fluorescent. In the rare earths and uranyl compounds, the narrowness of the absorption bands has been held to indicate that the electron transfer process is well protected against fluorescence. Although this seems true also of chloropyhll and porphyrins, it does not apply to many dyes, such as uranin or trypaflavin, so that it is improbable that there can be a definite correlation between the fluorescence of a compound and the width of its absorption bands. Furthermore, there seems to be no parallelism between the electrical conductivity of a dye and its fluorescence, although it is true that, as in the case of fluorescent indicators, the absorption spectra and fluorescence may vary with the state of ionization of the dye. Weiss[36] believes that all organic molecules with strong fluorescence have conjugated band systems in which the excitation energy is not easily transformed into heat, or in other words, that there is no coupling between free electrons of these systems and the vibrations of the heavy particles. Mumm[38] regards the fluorescent substance as an intermediate state (resonance form) between two end structures. Absorption raises an electron to an excited state from which it drops to one of the end states with the appearance of fluorescence. This end structure then passes to the intermediate state with evolution of heat. He has applied this theory, developed for N-methyl-α-pyridones, to the fluorescence of barium platinocyanide and to uranyl salts.

A number of studies have been concerned with the measurement of the fluorescence efficiency of dyes and other substances. Some materials, as solid anthracene, have high efficiencies approximating unity. In various solvents, however, anthracene has maximal efficiencies which vary from 0.28 to 0.01. Bowen and Norton[39]

[34] Noack, K., *Naturwiss.*, **14**, 383 (1926); *Chem. Abs.*, **20**, 2521 (1926); **21**, 2011 (1927); *Biochem. Z.*, **183**, 144 (1927); Gaffron, H., *Biochem. Z.*, **179**, 157 (1926).

[35] Shpol'skiĭ, E., and Sheremet'ev, G., *J. Phys. Chem. (U.S.S.R.)*, **8**, 640 (1936); *Chem. Abs.*, **31**, 2100 (1937).

[36] *Trans. Faraday Soc.*, **35**, 15 (1939).

[37] Pringsheim, P., *Ibid.*, **35**, 28 (1939).

[38] Mumm, O., *Ber.*, **72B**, 29 (1939). For an earlier discussion of theories of fluorescence, see Perrin, F., *Ann. Physique*, **12**, 169 (1929).

[39] Bowen, E. J., and Norton, A., *Trans. Faraday Soc.*, **35**, 44 (1939).

find that the fluorescence efficiency F depends on the nature of the fluorescent substance, the solvent, concentration of solute, temperature and concentration c of quencher. It may be expressed by $F=\frac{k_1}{1+k_2C}$ in which k_1 and k_2 are constants. Many processes tend to lower the efficiency in solution. Some, such as an inner filtering action of some solute or of the solvent, or the formation of non-fluorescent compounds with the solvent, or the formation of aggregates,[40] do not appear to be related to true quenching processes. The progressive introduction of halogens into such a dye as fluorescein diminishes the fluorescence; for this the somewhat misleading term "internal quenching" has been suggested.

True quenching of fluorescence in solution refers to a process in which the excitation energy absorbed by a certain percentage of the absorbing molecules may be transferred to other molecules before it can be emitted as light.[41] Two types have been distinguished. The quenching is said to be static when the quenching molecule is within the sphere of action of the fluorescent molecule during the absorption process. When the quencher must diffuse toward the excited molecule during its lifetime, the quenching is said to be diffusional. Many strong quenchers of dye fluorescence act in this manner.

The quencher may be an inorganic ion, as studied by West, Müller and Jette,[42] a foreign molecule as oxygen, or even other molecules of the fluorescent substance. If the latter, the process of quenching (self-extinction) generally causes the fluorescence intensity to decrease with an increasing concentration of the dye. Self-extinction may be regarded as due to collisions of the second kind between like molecules. Kautsky,[43] however, claims that this is incorrect and that self-extinction is due to a lengthening of the life of the excited molecules. This view is based chiefly upon observations of fluorescent solids which show increased phosphorescence with decreased fluorescence. Kautsky claims that in liquids long-lived states may be produced, although the phosphorescence lasts but 10^{-3} sec. because of the greater ease of the conversion of excitation energy into thermal energy. Concentration quenching occurs at such low concentrations as 10^{-4} mole per liter in the case of anthracene solutions. Pringsheim points out that this could scarcely be accounted for by energy resonance between excited and unexcited molecules. He suggests that it may more likely be related to a utilization of part of the energy in some photochemical change, the excess being converted into heat. In the case of anthracene, the reaction is the formation of dianthracene (Chapter 26). The self-extinction of fluorescence is also encountered in the case of the photochemical reactions of other hydrocarbons with condensed ring systems.

Other molecules, *e.g.*, non-fluorescent dyes, with absorption bands overlapping those of the fluorescent substance, act as strong quenchers. Many antioxidants,[44] phenols, amines and the iodide ion act as quenchers. In such cases, little is known of the mechanism of quenching. Most quenchers act only after many collisions and in some cases it is believed that the quenching is stepwise. Since the temperature has little influence, no activation seems necessary.

In the Faraday Society discussion, D. D. Eley suggested that the magnetic

[40] Kortüm, G., *Z. physik. Chem.*, **33B**, 1 (1936); **34B**, 255 (1936); Lewschin, W. L., *Acta Physicochim. U.S.S.R.*, **2**, 221 (1935); *Chem. Abs.*, **29**, 7798 (1935).

[41] Franck, J. M., and Wawilow, S. J., *Z. Physik.*, **69**, 100 (1931); Sveshnikov, B., *Acta Physicochim. U.R.S.S.*, **3**, 257 (1935); **4**, 453 (1936); **7**, 755 (1937); *Chem. Abs.*, **30**, 3327 (1936); **31**, 5681 (1937); **32**, 4880 (1938).

[42] West, W., Müller, R. H., and Jette, E., *Proc. Roy. Soc. London*, **121A**, 294, 299, 313 (1928).

[43] Kautsky, H., and Merkel, H., *Naturwiss.*, **27**, 195 (1939).

[44] Perrin, J., *Compt. rend.*, **184**, 1097 (1927); Privault, *Ibid.*, **184**, 1120 (1927).

effect of such paramagnetic ions as Fe^{++}, Ni^{++}, Cu^{++} may quench the fluorescence of porphyrins by a magnetic predissociation process. Halide ions might also quench dyes by a predissociation process induced by their electric fields did their hydration envelopes not prevent the ions from approaching closely enough. Weiss, however, showed that strong magnetic fields do not affect the fluorescence of dye solutions, and believed the halide ions to act by a radiationless transfer of an electron from the ion to the excited dye. This theory may be compared with the view of Hachkowskiĭ and Terenin[45] that molecules adsorbed on fluorescent solids quench by taking up free electrons from the solids to form negative ions.

Weiss[46] has developed his theory in considerable detail and employed it to interpret a number of experimental observations. The irradiation with a 1500-watt carbon arc of a methylene blue solution in the presence of the ferrous ion, causes a bleaching which is reversed when the irradiation ceases.

$$M\,B + 2Fe^{++} + 2H^+ \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} \underbrace{M\,B,H_2}_{\text{leuco-dye.}} + 2Fe^{+++}$$

Although the iodide ion had no similar effect on methylene blue, it did cause a bleaching action, proportional to the square root of the light intensity, on Lauth's violet and a slight one on eosin. Weiss holds that when an excited dye molecule D* collides with an acceptor molecule or ion which has an electron in a level corresponding to that left vacant by the electronic shift in the dye excitation, the electron passes to the excited dye, forming the non-fluorescent excited D^-.

$$D^* + \text{Accep.} \rightleftarrows D^- + \text{Accept}^+$$
$$D^* + I^- \rightleftarrows D^- + I$$
$$D^* + Fe^{++} \rightleftarrows D^- + Fe^{+++}$$

A quantum mechanical resonance between the states (D*, Accep) and (D^-, Accept^+) is assumed. The dye molecule with the electron thus acquired may then on combination with a proton form a semiquinone DH, two molecules of which react to form the leucobase and oxidized dye.

$$D^- + H^+ \longrightarrow DH$$
$$2DH \longrightarrow DH_2 + D.$$

It was possible to develop mathematical relations between the relative effectiveness of various halogen ions in quenching dye fluorescence and their electron affinities.[47]

The reactions described may also be used to explain the dye-photosensitized oxidation of larger quantities of ferrous ion, iodide ion or other acceptor, since when the semiquinone or leucobase has been formed, it can be reoxidized thermally to the dye by the air and thus be made capable of oxidizing more of the acceptor.

It will be noted that this theory takes no account of any effect which oxygen itself may have upon the fluorescence of the dye.[48] It has, however, been demonstrated that the fluorescence of chlorophyll or hematoporphyrin can be quenched by molecular oxygen, and cannot be quenched by acceptors, such as thiosinamine or

[45] Hachkowskiĭ, V., and Terenin, A., *Acta Physicochim. U.R.S.S.*, **7**, 521 (1937).

[46] Weiss, J., *Trans. Faraday Soc.*, **32**, 1331 (1937); **35**, 48 (1939); *Nature*, **135**, 648 (1934); **136**, 794 (1935); Weiss, J., and Fishgold, H., *Z. physik. Chem.*, **32B**, 135 (1936); *Nature*, **137**, 71 (1936).

[47] See also Weber, K., *Z. physik. Chem.*, **30B**, 69 (1935).

[48] Schneider, E., *Z. physik. Chem.*, **28B**, 311 (1935).

isoamylamine. Such observations led Kautsky [49] to propose a different theory of photosensitized oxidations according to which it is assumed that collision with an excited dye molecule raises an oxygen molecule into a metastable excited state. Gaffron [50] disagreed with this (for further details see Chapter 44) and Franck and Levi [51] suggested that the HO_2 molecule may be formed in the quenching process and subsequently react with an acceptor. Weiss suggests the possibility of the O_2^- ion instead, believing its formation especially likely in the case of the collision of an oxygen molecule with an absorbed and excited dye such as trypaflavine.[52]

In his most recent work, Kautsky [53] studies particularly the phosphorescence of dyestuffs adsorbed on silica or alumina gels and maintained in an evacuated vessel. The phosphorescence is said to be quenched by oxygen independently of its pressure down to a few thousandths of a mm. The quenching of the fluorescence, however, is said to depend upon the oxygen pressure. Kautsky interprets these experiments as favoring the formation of metastable oxygen molecules, since he could detect their diffusion by the following method. A mixture of fine grains of silica gel with adsorbed sensitizer and larger grains of silica gel with adsorbed leuco-methylene blue became blue when the oxygen pressure was made just small enough to quench the fluorescence of the sensitizer. When both the sensitizer and the acceptor are adsorbed on the same surface, the diffusion path is shortened and in light the color becomes blue at pressures up to one atmosphere. Such a mixed adsorbate is regarded as representing a transition to the conditions encountered in solution. An essential feature of Kautsky's theory is the phosphorescence, some oxygen-free solutions of sensitizers being reported to exhibit light for as long as 10^{-2} sec., after illumination, whereas the life of the usual excited state which causes fluorescence is only of the order of 10^{-8} sec. This phosphorescence, the yield of which is small, is thought to occur only in regions where there is slight association of the dye molecules. This afterglow is thought to be due to metastable excited states of dyes capable of causing but weak fluorescence. The afterglow can be demonstrated by the addition to 20 cc. of acetone of two to four drops of a 0.006 molar solution of any such efficient photosensitizers of oxidation as isoquinoline red, benzoflavine, eosin, hematoporphyrin, chlorophyll, erythrosin, phloxin or rose Bengal.[54] Strongly fluorescent compounds do not exhibit it under these conditions. A very small concentration of oxygen inhibits the afterglow, but the oxygen acceptors, thiosinamine and isoamylamine, have no effect.

Scheibe [55] suggests that in solution certain dyes may occur as polymers of several hundred molecules. The polymer may absorb many quanta simultaneously. This energy may be lost by fluorescence or by collision with a foreign molecule which may thus acquire a very large number of quanta, resulting in the formation of short-lived intermediate products at energy levels which could never be attained by the direct absorption of light.

Claims of the existence of a negative photosensitization have been made. Milbauer [56] observed that in the presence of 0.02, 0.2 or 1.0 mg. of the dyes Nile blue, Brilliant Green, Capri Blue, phenosafranine, fuchsin, pinacryptol green or

[49] Kautsky, H., and de Bruijn, H., *Naturwiss.*, **19**, 1043 (1931); Kautsky, H., *Ber.*, **65**, 1762 (1932); *Trans. Faraday Soc.*, **35**, 216 (1939).
[50] Gaffron, H., *Biochem. Z.*, **264**, 251 (1933); *Ber.*, **68**, 1409 (1935).
[51] Franck, J., and Levi, H., *Naturwiss.*, **23**, 229 (1935).
[52] See Pringsheim, P., and Vogels, H., *J. chim. phys.*, **33**, 345 (1936).
[53] Kautsky, H., *Trans. Faraday Soc.*, **35**, 216 (1939).
[54] Kautsky, H., Hirsch, A., and Flesch, W., *Ber.*, **68B**, 152 (1935).
[55] Scheibe, G., *Naturwiss.*, **25**, 795 (1937).
[56] Milbauer, J., *Chem. Listy*, **29**, 267 (1935); *Phot. Korr.*, **71**, 94; *Chem. Abs.*, **30**, 1661 (1936).

methylene violet per 10 cc., the rate of decomposition of an active methanol solution containing 28.2 gm. per liter of sodium N-chloro-*p*-toluenesulfonamide is slower than in their absence, when exposed to intense visible light. Since simultaneous experiments with these dye mixtures in darkness did not show a loss of activated chlorine, it was believed that a negative photocatalysis had been demonstrated. In the same range of concentrations, malachite green, pinacryptol yellow and methylene blue did not exhibit this phenomenon, for in darkness they consumed activated chlorine and were themselves decomposed.

A more complete discussion of the phenomena of luminescence and phosphorescence lies beyond the scope of this book, although in some instances ultraviolet radiations may be employed in eliciting these phenomena. Some developments of the earlier work in these fields led to significant work on the nature of the coloration produced in alkali halide crystals by irradiation. These are discussed in Chapter 21. A general discussion of the mechanism of phosphorescence has been given by Pohl.[57] A phosphor may be defined as an insulating crystalline material into which a minute trace of a highly refracting substance has been incorporated in the molten state. Excitation consists in the liberation of electron by photoelectric effects; luminosity arises from the return of such electrons to the normal state.

Chemoluminescence. This phenomenon represents, in a way, the converse of a photochemical change or of a photosensitized reaction. It is a process in which light is evolved during the course of a chemical reaction; the efficiency is seldom more than 1 per cent. Limitations of space prevent the discussion of this topic. For recent discussions, see Kautsky,[58] Nichols,[59] Beutler,[60] and a report of the National Research Council.[61]

Photochemical Reactions in Surfaces

Recently an attempt has been made to develop the theory that the velocity of photochemical reactions conducted in mono- or multi-molecular layers at the surface of a liquid depends upon the molecular orientation of the absorbing molecules.[62] Among the reactions studied have been the hydrolysis of stearic anilide spread on half-normal sulfuric acid, the decomposition of α-hydroxystearic acid with liberation of carbon dioxide produced by wave-lengths shorter than 2480A, the oxidation and hydrolysis of proteins, etc. The effects of traces of such sensitizers as nickel and copper and of inhibitors as potassium cyanide is, in some cases, pronounced.

On glass of refractive index 1.5, invisible multilayers of barium acid stearate (containing equal parts of stearic acid and barium stearate in each) when irradiated by a high-pressure mercury arc showed interference colors. Five minutes of irradiation of a 48-layer film caused a loss of optical thickness which amounted to one layer.[63] The loss continued for several hours after the irradiation had been stopped, finally amounting to more than two layers. A similar change occurs in pure stearic acid layers, but barium stearate shows only one twentieth this loss.

[57] Pohl, R. W., *Naturwiss.*, **16**, 477 (1928); see also Melville, H. W., *Science Progress*, **33**, 527 (1939); Leverenz, H. W., and Seitz, F., *J. Applied Physics*, **10**, 479 (1939); Symposium on Luminescence, *Trans. Faraday Soc.*, **35**, 2 (1939).
[58] Kautsky, H., *Trans. Faraday Soc.*, **21**, 591 (1925).
[59] Nichols, E. L., *J. Opt. Soc. Am.*, **20**, 106 (1930).
[60] Beutler, H., *Angew. Chem.*, **45**, 249 (1932); Beutler, H., and Polanyi, M., *Z. Physik*, **47**, 379 (1928).
[61] *Bull. Nat. Research Council*, **59**, 30 (1927).
[62] Mitchell, J. S., *J. Chem. Physics*, **4**, 725 (1936); **5**, 83 (1937); Mitchell, J. S., Rideal, E. K., and Schulman, J. H., *Nature*, **139**, 625 (1937); Rideal, E. K., and Mitchell, J. S., *Proc. Roy. Soc. London*, **159A**, 206 (1937).
[63] Schaefer, V. J., *Science*, **89**, 465 (1939).

It is believed that radiations of 2300-2700A split the molecules of stearic acid at the attachment of the carboxyl group.

Photochemistry and Optical Activity

There have been many attempts to prepare optically active substances by methods such that the form with one configuration results in larger amount than its antipode. One of the first successful experiments was performed in 1930 by Kuhn and Knopf.[64] It involved the use of circularly polarized light in causing the decomposition of α-azidopropiondimethylamide. This compound has an absorption band at about 2900A with a strong anisotropic factor of 0.02-0.03.[65] When acted upon in hexane solution by circularly polarized light of this wave-length, it undergoes decomposition of the azido-group, one stereoisomer being decomposed to a greater extent than the other. This is because the difference between the absorption coefficients of the compound for right and left circularly polarized light is, as stated, about 2 to 3 per cent. From the amount of nitrogen liberated, it was shown that the reaction follows approximately the Einstein equivalence law. The unchanged dimethylamide can be separated from the reaction products by distillation. When 40 per cent of the original racemic compound had been decomposed, the remainder showed in a 10-cm. polariscope tube a rotation of +0.78° when the irradiation had been conducted with *d*-circularly polarized light and of −1.04° when *l*-circularly polarized light had been used. The order of magnitude of these effects was in agreement with theoretical predictions. Kuhn, with Braun[66] had made earlier similar observations on ethyl α-bromopropionate in which near ultraviolet bands powerfully influence the optical activity.

Important earlier contributions to the field of asymmetric synthesis employing circularly polarized light and magnetic fields were made by Cotton.[67] In these experiments, active molecules were not, however, produced, as there resulted only an active arrangement of the molecules in a medium.[68] Studies of the photodichroism and photoanisotropy of light-sensitive solid layers of a gelatin photographic emulsion have been made by Weigert.[69] The primary action in induced photodichroism is assumed to be the deformation of micelles held together by van der Waals forces. The form of the spheres detached within the micelles depends on the wave-form of the exciting light.[70]

There have been other recent attempts to obtain a total asymmetric synthesis. Davis and Haggie[71] reported the production of optically active trinitrostilbene dibromide by the photobromination of 2,4,6-trinitrostilbene by circularly polarized light of wave-lengths 3600 to 4500A. As solvents, they used carbon tetrachloride, benzene, glacial acetic acid and nitrobenzene. The last was the most suitable. In every case the reaction mixture assumed an optical activity which increased to a maximum and then decreased slowly and finally disappeared as the reaction

[64] Kuhn, W., and Knopf, E., *Naturwiss.*, **18**, 183 (1930); *Z. physik. Chem.*, **7B**, 292 (1930); *Ber.*, **63B**, 190 (1930).

[65] The theory of the relation between circular dichroism and optical rotatory power within and without absorption bands previously developed by Kuhn, W., *Z. physik. Chem.*, **4B**, 14 (1929) led to this work.

[66] Kuhn, W., and Braun, E., *Naturwiss.*, **17**, 227 (1929).

[67] Cotton, A., *Compt. rend.*, **189**, 657 (1929).

[68] See also Zocher, H., and Koper, K., *Z. physik. Chem.*, **132**, 295, 302, 313 (1928); Bruhat, G., *Bull. soc. chim.*, **47**, 251 (1930).

[69] Weigert, F., *Z. physik. Chem.*, **3B**, 377, 389 (1929); **4B**, 83 (1929). See also Chapter 21.

[70] Weigert, F., *Z. physik. Chem.*, **10B**, 241 (1930); Ghosh, J. C., *J. Indian Chem. Soc.*, **16**, 51 (1939); *Chem. Abs.*, **33**, 5744 (1939).

[71] Davis, T. L., and Haggie, R., *J. Am. Chem. Soc.*, **57**, 377 (1935).

proceeded to completion. Since the product on standing, whether in ordinary or in polarized light, loses its optical activity and since this cannot be restored by further exposure to polarized light, it was inferred that optical activity arises at the moment of the synthesis of the compound. The degree of rotation secured, although small (0.04°), was beyond the limit of error of the observations. The reaction is a chain, initiated by excited bromine atoms in which activated trinitrostilbene molecules may or may not take part. In diffused daylight or in unpolarized light, the reaction failed to form optically active material. Optically inactive trinitrostilbene dibromide is not rendered active by exposure of its solutions in nitrobenzene to circularly polarized light. In these experiments, the circularly polarized light was obtained by reflecting the light of a glass-enclosed mercury arc filtered through blue cobalt glass at the polarizing angle from a plate of black glass and by passage through a thin sheet of mica. No optically active product could be obtained by the use of circularly polarized light of wave-length 5890-5896A. The formation of optically active material was also observed when chlorine reacted with trinitrostilbene in nitrobenzene solution in circularly polarized light of wave-lengths between 3600 and 4500A. The reaction was much faster than in the case of bromine but no greater activity could be obtained. Maximum rotations were obtained in about 45 minutes.

Attempts of this sort had been previously made by Ghosh and Purkayastha[72] in the bromination of stilbene and of cinnamic acid, but the formation of optically active materials was not described. They found for the same intensities, ordinary light and plane polarized light to be equally effective, and circularly polarized light slightly less so. In the decomposition of potassium manganioxalate, however, it was slightly more effective than either non-polarized or plane-polarized light.[73]

By irradiating methyl (4-methylphenyl) (*p*-ethylphenyl)trimethylmethane with circularly polarized light of 4300A while introducing chlorine at 0°, Karagunis and Drikes[74] claimed to have obtained an optical rotation of 0.1° When light (5890A) which lies within the absorption band was used, the opposite rotation appeared.

Observations by Baly and Semmens[75] regarding the action of plane polarized light in hydrolyzing starch in plant leaves stimulated a large amount of work in which it was attempted to show that polarized light is more effective than ordinary light in effecting various photochemical reactions. Whatever may subsequently be found in regard to the action of plane polarized light upon substrates the molecules of which are definitely oriented in surface layers, in solids or in biological structures, there is no reason to expect it to be more effective than ordinary light of equal intensity in effecting photochemical reactions in solutions in which the substrate molecules have a random orientation. It has been shown by Bhatnagar, Anand and Gupta[76] that no differences are to be observed in the photochemical reactions by polarized and ordinary light between diammonium oxalate and mercuric chloride or in the decomposition of alkaline hydrogen peroxide.

Nevertheless, it has been claimed[77] that polarized light produces changes in the

[72] Ghosh, J. C., and Purkayastha, R. M., *Quart. J. Indian Chem. Soc.*, **2**, 261 (1925); *Chem. Abs.*, **20**, 1953 (1926).

[73] Ghosh, J. C., and Kappanna, A. N., *Quart. J. Indian Chem. Soc.*, **3**, 127 (1926); *Chem. Abs.*, **20**, 3646 (1926).

[74] Karagunis, G., and Drikes, O., *Naturwiss.*, **21**, 607 (1933); *Chem. Abs.*, **28**, 144 (1934).

[75] Baly, E. C. C., and Semmens, E. S., *Proc. Roy. Soc. London*, **97B**, 250 (1924).

[76] Bhatnagar, S. S., Anand, H. L., and Gupta, A. W., *J. Indian Chem. Soc.*, **5**, 49 (1928); *Chem. Abs.*, **22**, 3840 (1928). Zhalkovskii, B. G., *Bull. biol. med. exptl. U.R.S.S.*, **5**, 493 (1938); *Chem. Abs.*, **33**, 2544 (1939). See also Bhatnagar, S. S., Lal, R. B., and Mathur, K., *Nature*, **118**, 11 (1926) for physiological effects claimed to be due to polarized light.

pharmacological properties of a number of drugs not produced by irradiation with non-polarized light. Irradiation of tincture of digitalis with polarized light was said to produce a deterioration as shown by a weakened pharmacological action. When ultraviolet light is used a further change or decomposition occurs and the tincture becomes more poisonous. With digitalis, it was claimed that circularly polarized light produced even greater deterioration than did plane polarized light. Macht and Krantz [78] stated that in these experiments the test and control solutions were simultaneously irradiated with polarized and non-polarized light of equal intensity.

On the other hand, Dailey and Benedict [79] were unable to show that polarized light had any selective action in the decomposition of cocaine hydrochloride, when irradiation times of from one to twelve hours were employed. This is at present generally believed to be true of photochemical reactions of substances under conditions in which they are capable of free and random orientation. Other workers to deny the claims for a special effectiveness of polarized light have been Bunker and Anderson [80] and Bond and Gray.[81]

Phototropy

This term refers to a change in color suffered by a solid on exposure to light, which is slowly reversed when the solid is subsequently kept in darkness. It was first observed, named and extensively investigated by Marckwald.[82] It is exhibited by over two hundred substances, but as yet little quantitative work has been done. An interesting feature is the occurrence of phototropic fatigue. 3,5-dibenzoyl-2,4,4,6-tetraphenyltetrahydropyran, which is colorless in the dark, becomes violet on exposure to light, especially that of short wave-lengths. It again becomes colorless after some hours or days in darkness. After ten such colorations and decolorations, however, it loses its phototropic properties and its melting point falls from 235-6° to 225°C.[83] In solution, it is insensitive to light, and the colored form when dissolved yields colorless solutions. An occasional instance of phototropy in solution has, however, been reported. Singh [84] observed a green color to develop in chloroform solutions of α-naphthylaminocamphor on exposure to direct sunlight, followed by a much slower reversal in darkness. The coloration was accompanied by a large increase in optical rotation. The addition of a trace of sodium ethoxide prevented the appearance of the green color. The results were tentatively attributed to the formation of a compound from the keto and enol modifications.

The phototropy of inorganic compounds of the type $2HgS.HgX_2$ or 2HgS.HgX has been attributed [85] to their dissociation into the simple component salts, recombination occurring in darkness with the reëmission of radiant energy.

[77] Macht, D. I., and Anderson, W. T., Jr., *J. Am. Chem. Soc.*, **49**, 2017 (1927).
[78] Macht, D. I., and Krantz, J. C., Jr., *J. Am. Pharm. Assoc.*, **16**, 106 (1927).
[79] Dailey, H. T., and Benedict, H. C., *J. Am. Chem. Soc.*, **51**, 808 (1929).
[80] Bunker, J. W. M., and Anderson, E. G. E., *J. Biol. Chem.*, **77**, 473 (1928).
[81] Bond, W. R., and Gray, E. W., *J. Pharm. Exp. Therap.*, **32**, 351 (1928). See also for further details of the controversy, Jones, W. N., *Ann. Botany*, **39**, 651 (1925); Baly, E. C. C., and Semmens, E. S., *Nature*, **116**, 817 (1925); Semmens, E. S., *Plant Physiol.*, **1**, 201 (1926); *Nature*, **117**, 821 (1926); Lord Rayleigh, *Nature*, **117**, 15 (1926); Navez, A. E., and Rubenstein, B. B., *J. Biol. Chem.*, **80**, 503 (1928).
[82] Marckwald, W., *Z. physik. Chem.*, **30**, 140 (1899). For reviews, see Gallagher, P., *Bull. soc. chim.*, **29**, 683 (1921) and Chalkley, L., Jr., *Chem. Rev.*, **6**, 217 (1929). Note also Bhatnagar, S. S., Kapur, P. L., and Hashmi, M. S., *J. Indian Chem. Soc.*, **15**, 573 (1938); *Chem. Abs.*, **33**, 3698 (1939).
[83] de Carvalho, A. P., *Compt. rend.*, **200**, 60 (1935).
[84] Singh, B. K., *Quart. J. Indian Chem. Soc.*, **1**, 45 (1924); *Chem. Abs.*, **19**, 935 (1925).
[85] Rao, E. L., Varahalu, K., and Narasimhaswami, M. V., *Nature*, **124**, 303 (1929).

Photoelectric Phenomena

In 1839, Becquerel [86] discovered that when one of two platinum or silver electrodes in dilute sulfuric acid is illuminated, an electromotive force is set up by the cell. That the conductivity of certain substances, notably selenium, is affected by light was, according to Bidwell [87] discovered by Willoughby Smith in 1873. In attempting to explain an observation by Hertz [88] that ultraviolet illumination of a spark gap permits the passage of a longer spark, Hallwachs [89] discovered the emission of negative electricity from a surface irradiated by ultraviolet rays. As pointed out by Hughes and DuBridge,[90] these three phenomena are separate manifestations of photoelectric processes, which all depend upon the ability of light to release electrons from matter.

Historically, the photoelectric effect is of the greatest importance, since it was the study of this phenomenon which enabled Einstein [91] to reveal the fact that the interaction between matter and radiation must be explained in terms of quanta of radiation. The theoretical structure of modern photochemistry is based upon his introduction of the concept which led to the logical development of the photochemical equivalence law. On the other hand, the actual occurrence of a photoelectric effect as a part of the mechanism of photochemical processes is relatively unusual. That air and other gases may be ionized by ultraviolet radiations has long been recognized [92] and at one time it was believed that photoionization might play an important role in photochemical processes. But when the amounts of energy required to ionize the molecules of various gases became known, it became evident that the wave-lengths corresponding to ionization are generally far shorter than those required to bring about most photochemical processes. Only rays passing through fluorite are able to ionize most gases. The required thresholds range from 1300A for nitric oxide to 760A for nitrogen, the halogens having the values chlorine, 940A, bromine, 970A, and iodine, 1230A.[93]

Many investigations have been made of the effects of illumination upon the electrodes of electrolytic or voltaic cells, but these lie beyond the scope of this work.

[86] Becquerel, E., *Compt. rend.*, **9**, 145, 561 (1939); for a recent review, see Stora, C., *J. chim. phys.*, **34**, 536 (1937).
[87] Bidwell, S., *Phil. Mag.*, **20**, 178 (1885).
[88] Hertz, H., *Ann. Physik*, **31**, 983 (1887).
[89] Hallwachs, W., *Ann. Physik*, **33**, 301 (1888).
[90] Hughes, A. L., and DuBridge, L. A., "Photoelectric Phenomena," New York, McGraw-Hill Book Co., 1932.
[91] Einstein, A., *Ann. Physik*, **17**, 132 (1905).
[92] Thomson, J. J., *Proc. Cambridge Phil. Soc.*, **14**, 417 (1907); *Chem. Abs.*, **2**, 1656 (1908).
[93] See Mackay, C. A., *Phil. Mag.*, **46**, 828 (1923); Morris, J. C., Jr., *Phys. Rev.*, **32**, 456 (1928); Hughes, A. L., and DuBridge, L. A., "Photoelectric Phenomena," p. 274, New York, McGraw-Hill Book Co., 1932.

Chapter 17

Reactions of Inorganic Gases: Hydrogen Halides

In Chapter 14 it was shown that a knowledge of the spectrum of a gas is essential to comprehending the reactions which it may undergo under the influence of radiations. Even when apparatus capable of revealing the finer structure of the molecular spectra is not available, crude spectrographs may furnish an indication of the wave-length regions within which the gas absorbs and will therefore give some indication of the regions within which photochemical reactions can occur. A brief discussion of the manner in which absorption measurements are made will first be given. Then in the discussions of the individual reactions, the absorption spectrum of each of the components will be described in order that the findings of spectroscopy as to the nature of the possible primary processes may furnish a guide for a critical appraisal of the various speculations proposed in explanation of the reported observations on the kinetics of the reactions.

The Measurement of Ultraviolet Absorption Spectra of Gases or Liquids

Since this is not a text of laboratory procedure, only principles and not details of technique will be mentioned. In general, the methods are similar to those commonly employed in the visible region. Ultraviolet light, from a spark source or hydrogen discharge tube, is divided into two parallel paths, one of which passes directly into the spectrograph; the other passes through a cell containing the gas or the solution the absorption of which is to be measured. (If the absorption of a solution is being studied, the first beam should pass through a cell containing the pure solvent.) The two spectra are then photographed side by side. Several exposures are made on adjacent portions of the photographic plate, the intensity of the comparison beam being varied to a known extent in each. Methods employed in photometers for decreasing the intensity of the comparison beam include the interposition of rotating sectors which vary in known manner the duration of intermittent exposures, the use of wire screens [1] or calibrated platinum wedges deposited on quartz, Nicol polarizing prisms or variations of the aperture admitting the comparison beam (Spekker method of Adam Hilger, Ltd.). It would theoretically be best to secure the variation in intensity by varying the distance from the source, but this is not feasible when a photographic method is employed and it has rarely been used in other methods.[2]

In each of the series of double spectra, however obtained, there are located (visually or microphotometrically) the wave-length regions at which there is agreement between the intensity of the light passing through the absorption cell and that coming directly from the source. The wave-lengths corresponding to various positions along the spectrum are determined by a simultaneously photographed scale embodied in the instrument or located by the use of known lines of the source as landmarks. Most of the methods in common use, particularly for

[1] Winther, C., *Z. wiss. Phot.*, **22**, 125 (1923); Landsberg, G. S., *Z. Physik*, **46**, 106 (1927).

[2] Schaefer, K., *Z. angew. Chem.*, **33**, 25 (1920).

work with solutions, involve merely a direct visual matching of the intensities upon the photographic plate variously illuminated.

A method in which the light intensity was kept constant and the path of absorbent traversed, or the concentration of the absorbing solution, was varied, was introduced by Henri.[3] Refinements in this method have been introduced by de Lazlo.[4] A simple method employing only a quartz spectrograph and no photometer has been employed by Loofbourow.[5] Methods have also been devised employing but one beam of light, so that instead of matching intensities on a photographic plate, the energy of the beam is measured by a thermopile or, more usually, a photoelectric cell and accessory apparatus, with the absorption cell in the beam and without it. Among photoelectric spectrophotometric methods are those of Hogness, Zscheile and Sidwell.[6] Automatic recording devices have also been constructed. A continuous representation of the absorption curve of a rapidly changing system can be obtained by the aid of a cathode-ray oscillograph, according to Holiday and Smith.[7] The fine structure of the absorption spectra of gases is obtained by micrometric tracings of photographed spectra.[8]

In the absorption curve of a substance there is plotted against wave-lengths as abscissae the ratio of the light passing through the absorbing substance (I_x) to that incident upon it (I_0). This ratio is given by the logarithmic relation $I_x/I_0 = e^{-kcd}$, in which c is the concentration of a solution (or pressure of a gas), d the thickness of the absorbing layer and k is a constant characterizing the absorption of the substance at the wave-length in question. A plot of k against the wave-lengths gives graphically the absorption of the substance throughout the spectral range investigated. k is known as the absorption coefficient, and varies with the wave-length. The numerical value of k is obtained by dividing the product cd into the natural logarithm of the ratio of I_0/I_x. In practice, most workers employ the more convenient common logarithms. The terms "extinction coefficient" and "absorption coefficient" are rather indiscriminately employed to designate the values obtained by the use of either logarithmic base. In general, German authors follow Kayser in using the term "absorption coefficient" for values based on natural logarithms and English workers follow Bunsen and Roscoe in using "extinction coefficient" for values based on the use of logarithms to the base ten. The distinction in terms is by no means universally observed.

[3] See Ley, H., and Volbert, F., *Z. wiss. Phot.*, **23**, 41 (1924).

[4] de Lazlo, H., *J. Phys. Chem.*, **32**, 505 (1928).

[5] Loofbourow, J. R., *Bull. Basic Sci. Research*, **5**, 46 (1933).

[6] Hogness, T. R., Zscheile, F. P., Jr., and Sidwell, A. E., Jr., *J. Phys. Chem.*, **41**, 379 (1937).

[7] Holiday, E. R., and Smith, F., *Nature*, **134**, 102 (1934).

[8] See Harrington, E. A., *J. Opt. Soc. Am.*, **16**, 211 (1928); Gull, H. C., and Martin, A. E., *J. Sci. Instruments*, **12**, 379 (1935).

The following bibliography includes but a few of the more important papers on the measurement of absorption spectra and their applications to the study of constitution. A considerable proportion of them, indicated separately, are concerned primarily with the limitations of the photographic method because of the failure of the relation between the intensity of the light and the blackening of the plate.

van Halban, H., and Eisenbrand, J., *Proc. Roy. Soc.*, **116A**, 153 (1927); *Z. wiss. Phot.*, **25**, 138 (1928). Baly, E. C. C., and Riding, R. W., *Proc. Roy. Soc.*, **113A**, 709 (1927). Schaum, K., and Kellner, H. M., *Z. wiss. Phot.*, **24**, 85 (1926). Fromherz, H., *Z. physik. Chem.*, **1B**, 301 (1928). Gage, F. H., *J. Sci. Instruments*, **6**, 256 (1929). Conrad-Billroth, H., *Z. physik. Chem.*, **14B**, 122 (1931). Schlessinger, M., *Biochem. Z.*, **235**, 70 (1931). Ley, F., and Volbert, F., *Z. physik. Chem.*, **130**, 308 (1927). Twyman, F., *Proc. Phys. Soc. (London)*, **45**, 1 (1933). Ginsel, L. A., *Physica*, **3**, 578 (1936). von Halban, H., Kortüm, G., and Szigetti, B., *Z. Elektrochem.*, **42**, 628 (1936). Miller, E. S., *Plant Physiol.*, **12**, 667 (1937). Albers, V. M., and Knorr, H. V., *J. Opt. Soc. Am.*, **28**, 121 (1938). Deck, W., *Helv. Phys. Acta*, **11**, 1 (1937). Shlaer, S., *J. Opt. Soc. Am.*, **28**, 18 (1938). P. J. Kippen Zonen, *J. Sci. Instruments*, **15**, 141 (1938). Papers dealing with the limitations of the reciprocity law and the Schwarzschild law in photographic materials: Harrison, G. R., *J. Opt. Soc. Am.*, **11**, 341 (1925); **19**, 267 (1929). Kellner, H. M., *Z. wiss. Phot.*, **24**, 41, 79 (1926). Dorgelo, H. B., *Physik. Z.*, **26**, 756 (1925). Fabry, C., *Phot. J.*, **66**, 328 (1926). Jones, L. A., and Hall, V. C., *J. Opt. Soc. Am.*, **13**, 443 (1926). Webb, J. H., *J. Opt. Soc. Am.*, **23**, 316 (1933). Mees, C. E. K., *J. Opt. Soc. Am.*, **23**, 229 (1933). Harvey, A., *Science Progress*, **27**, 650 (1933). Kinele, H., *Naturwiss.*, **23**, 762 (1935). Pestemer, M., and Schmidt, G., *Monatsh.*, **69**, 399 (1936). Lambrey, M., and Corbière, J., *Compt. rend.*, **201**, 1351 (1935). van Kreveld, A., and Ornstein, L. S., *Proc. Acad. Sci. Amsterdam*, **39**, 478 (1936). de Langhe, J. E., *Physica*, **3**, 904 (1936). Kiss, A., and Gerendas, M., *Acta Lit. Sci. Regiae Univ. Hung. Francisco-Josephinae, Sect. Chem. Mineral. Phys.*, **5**, 153 (1937); *Chem. Abs.*, **32**, 1577 (1938).

The Formation and Decomposition of the Hydrogen Halides

The Decomposition of Hydrogen Iodide. According to Rollefson and Booher,[9] the first mention of this reaction was by Lemoine.[10] Also, the reaction was early studied by Bodenstein.[11] Warburg[12] found a quantum yield of approximately two for the wave-lengths 2070, 2530 and 2820A. In Chapter 12 it was shown that this observation could be accounted for equally well by either the mechanism of primary dissociation proposed by Warburg or of primary excitation of the hydrogen iodide molecule proposed by Stern and Volmer. Attempts to decide between the two by Bodenstein on the basis of kinetic measurements under varied experimental conditions, especially in the presence of foreign gases, were inconclusive. The data which eventually showed the correctness of the Warburg mechanism were predominantly physical and, as discussed in Chapter 14, came from the finding that the absorption spectrum of hydrogen iodide is continuous. At this point, we may consider in more detail the spectroscopic evidence regarding the absorption not only of hydrogen iodide but also of the products of the reaction, hydrogen and iodine.

Tingey and Gerke[13] found the absorption of hydrogen iodide to be entirely continuous and to begin at 3320A, corresponding to 86 kcal.; Coehn and Stuckardt[14] had previously placed this value at 3340A. It has been generally assumed[15] that the iodine atom produced in the dissociation is excited as in the case of the halogen from hydrogen chloride and hydrogen bromide. The energy of excitation of iodine is, from its atomic spectrum, 21.5 kcal. This, when subtracted from the energy corresponding to the long-wave threshold of the absorption spectrum 86 kcal. leaves 64.5 kcal., in fair agreement with the heat of dissociation of HI into normal atoms, 69 kcal. Goodeve and Taylor[16] calculated a potential energy curve for the upper state from the eigenfunction of the ground state and their own observations of the extinction values. Rollefson and Booher[17] found the absorption to extend as far as 3900A at least, and gave evidence that at 4120A, dissociation into normal atoms can occur; at 3120A, the iodine atom may be excited. Datta[18] places the absorption limit at 4040A.

Hydrogen. The fact that hydrogen absorbs only in the extreme ultraviolet range eliminates this substance as an absorbing component which might affect either the dissociation of hydrogen iodide or the combination of hydrogen and iodine. Dieke and Hopfield[19] found that in a 100 cm. layer at pressures of 2 to 50 mm. of mercury, hydrogen does not absorb wave-lengths longer than 1115A. Below this, it exhibits two band systems, the members of both of which converge at 849.4A to a region of continuous absorption corresponding to dissociation into a normal and an excited atom.

Iodine. Observations by Dymond[20] of the short wave-length limit of fluorescence were important in establishing the generally accepted interpretation of continuous spectra as indicative of dissociation. Iodine vapor exhibits bands which converge at 4989A to a continuous absorption region.[21] Fluorescence can be induced by wave-lengths longer than the convergence limit but cannot be observed in iodine vapor irradiated by wave-lengths within the continuous region. The dissociation produces a normal and an excited iodine atom.[22]

Extinction values have been given by Vogt and Königsberger[23] and, more recently, by Rabinowitsch and Wood.[24] The effect of varying the pressure of the iodine vapor has been studied by Perot and Collinet,[25] and the influence of foreign gases on the color of iodine vapor reported by Wright and McGregor.[26] The extinction coefficients drop off toward shorter wave-lengths in the continuous region. In the region below 2763A, iodine vapor exhibits a new region of banded absorption, the interpretation of which is not yet clear.[27]

By spectroscopic methods, Rabinowitsch and Wood[28] measured the quantum yield of the dissociation of iodine in the presence of foreign gases in three spectral regions. If the yield is unity in the continuum, it is 1.14 in the band region immediately on the long-wave side, and 1.10 at a point in the band region further from the limit. This indicates that all excited molecules dissociate by collisions with foreign molecules. Therefore, the quenching of the fluorescence is not due to the process $I_2^* + X \rightarrow I_2 + X$, but rather to $I_2^* + X \rightarrow I + I + X$. Quenching usually occurs at the first collision of an excited molecule with a foreign molecule, except in the case of helium which requires ten or more collisions before dissociation results. The atoms recombine mainly at the walls at low pressures. Under these conditions dissociation increases with the pressure. At higher pressures, however, the recombination occurs as a homogeneous reaction in the gas phase. The transition occurs sharply at 250 mm. in helium and 40 mm. in carbon dioxide. The dissociation is then proportional to the square root of the light intensity and to the inverse square root of the pressure, in accordance with the theoretical expression for recombination by three-body collisions. One double collision in 530 is a recombining one in helium and one in 50 in carbon dioxide at atmospheric pressure. The efficiency of the third body increases with its molecular size and with the intensity of the molecular fields of the colliding particles.

To decide between the mechanisms proposed (Chapter 12) for the decomposition of hydrogen iodide, Bonhoeffer and Farkas[29] studied the reaction at low pressures at which, were the reaction due to excited molecules, some re-radiation of the energy of excitation would be expected since the period between deactivating collisions would be longer than the life of the excited state. Since they could detect no fluorescence, it was concluded that the mechanism of Warburg (dissociation) must apply. Furthermore, exposure to light resulted in a fall of pressure

[9] Rollefson, G. K., and Booher, J. E., *J. Am. Chem. Soc.*, **53**, 1728 (1931).
[10] Lemoine, G., *Ann. Chim. Phys.*, **12**, 145 (1877).
[11] Bodenstein, M., *Z. physik. Chem.*, **22**, 23 (1897); **85**, 329 (1913); Bodenstein, M., and Lieneweg, F., *Z. physik. Chem.*, **119**, 123 (1926).
[12] Warburg, E., *Sitzb. preuss. Akad. Wiss.*, 314 (1916); 300 (1918).
[13] Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, **48**, 1838 (1926); see also Bonhoeffer, K. F., and Steiner, W., *Z. physik. Chem.*, **122**, 287 (1926); Lewis, B., *Nature*, **119**, 493 (1927).
[14] Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 722 (1916).
[15] Lewis, B., *Proc. Nat. Acad. Sci.*, **13**, 720 (1927); *J. Phys. Chem.*, **32**, 270 (1928).
[16] Goodeve, C. F., and Taylor, A. W. C., *Proc. Roy. Soc.*, **154A**, 181 (1936).
[17] Rollefson, G. K., and Booher, J. E., *J. Am. Chem. Soc.*, **53**, 1728 (1931).
[18] Datta, A. K., *Z. Physik*, **77**, 404 (1932).
[19] Dieke, G. H., and Hopfield, J. J., *Phys. Rev.*, **30**, 400 (1927); *Z. Physik*, **40**, 299 (1926).
[20] Dymond, E. G., *Z. Physik*, **34**, 553 (1925).

[21] Mecke, R., *Ann. Physik*, **71**, 104 (1923); Brown, W. G., *Phys. Rev.*, **38**, 709 (1931).
[22] Turner, L. A., *Phys. Rev.*, **27**, 397 (1926).
[23] Vogt, K., and Königsberger, J., *Z. Physik*, **13**, 292 (1923).
[24] Rabinowitsch, E., and Wood, W. C., *Trans. Faraday Soc.*, **32**, 540 (1936).
[25] Perot, A., and Collinet, M., *Compt. rend.*, **180**, 2030 (1925).
[26] Wright, R., and McGregor, T., *J. Chem. Soc.*, 1364 (1929).
[27] Pringsheim, P., and Rosen, B., *Z. Physik*, **50**, 1 (1928); Sponer, H., and Watson, W., *Ibid.*, **56**, 184 (1929); Kimura, M., and Miyanishi, M., *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **10**, 33 (1929). Further recent data on the absorption of iodine, particularly in the long-wave regions, have been given by Hirschlaff, E., *Z. Physik*, **75**, 315 (1932); Agarbiceanu, T., *Compt. rend.*, **194**, 702 (1932); Kondratjev, V., and Polak, L., *Physik. Z. Sowjetunion*, **4**, 764 (1933); Skorko, E., *Acta Phys. Polonica*, **3**, 191 (1934); Warren, D., *Phys. Rev.*, **47**, 1 (1935). The Budde effect differs from that of the other halogens in being proportional to the light intensity rather than to its 0.5 power. Narayana, T. S., *Indian J. Physics*, **9**, 111, 117 (1934); *Chem. Abs.*, **29**, 2847 (1935).
[28] Rabinowitsch, E., and Wood, W. C., *J. Chem. Physics*, **4**, 358, 497 (1936).
[29] Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **132**, 235 (1928).

which could be attributed only to the adsorption of free iodine atoms on the walls of the vessels. The same fall in pressure was also observed during the irradiation of hydrogen bromide.

Wave-lengths between 3000 and 2200A cause the complete decomposition of hydrogen iodide.[30] The velocity is independent of temperatures below 120°C.; it is lowered by addition of either iodine vapor or of an excess of hydrogen. At the beginning of reaction, the velocity remains constant for a time, then falls to that of a unimolecular reaction, and later falls again. The falling off in the rate toward the end of the decomposition is hastened when the initial pressure of hydrogen iodide is high and the temperature low. The initial reaction velocity appeared to increase approximately in proportion to the initial concentration of hydrogen iodide. Quantum yields somewhat higher than those of Warburg have been reported by Lewis,[31] his values being 2.36 for the 2080A and 2.35 for the 2530A zinc lines. The product of the intermediate reaction $H + HI \rightarrow H_2 + I$ is 25 per cent para-hydrogen at room temperatures. At 170°Abs. the hydrogen produced contains 2 per cent more para-hydrogen than does normal hydrogen.

Studies of the photochemical combination of hydrogen and iodine have been made by Coehn and Stuckardt,[32] who found that reaction can occur only in the ultraviolet region, and by Sasaki and Nakamura.[33] The latter workers found no combination could be induced by radiations longer than 3100A. It is suggested that hydrogen atoms may be produced by collisions of the second kind between hydrogen molecules and iodine molecules excited by the absorption of the 1800A line, although dissociation of iodine might be expected. The production of hydrogen atoms is essential that the reaction may go at ordinary temperatures since the reaction $I + H_2 \rightarrow HI + H$ is too endothermic to proceed. There is some evidence that the photocombination occurs under the influence of visible light at temperatures of 430-466°C.[34]

Other Halogen Hydrides.[35] Berthelot and Gaudechon[36] found that, as in the case of thermal decompositions, the stabilities of the hydrogen halides in light decrease with increasing atomic weights of the halogens. Those substances which require high temperatures for thermal decomposition require the shortest wave-lengths in the ultraviolet. For the decomposition of hydrogen chloride, wave-lengths shorter than 2000A are required to produce even a slow decomposition. Under similar conditions, hydrogen bromide is rapidly and completely decomposed. Coehn and Stuckardt[37] effected reactions of hydrogen halides from both

Table 19.—Photostationary States of Hydrogen Halides.

Acid	In quartz (2200A)	In Uviol glass (2500A)	In Jena glass (3000A)?
Hydriodic	92.2	100	100
Hydrobromic	100	about 20	0
Hydrochloric	0.42	0	0.

[30] Trautz, M., and Scheifele, B., *Z. wiss. Phot.*, **24**, 177 (1926).

[31] Lewis, B., *Proc. Nat. Acad. Sci.*, **13**, 720 (1927); *J. Phys. Chem.*, **32**, 270 (1928).

[32] Coehn, A., and Stuckardt, K., *Z. physikal. Chem.*, **91**, 722 (1916).

[33] Sasaki, N., and Nakamura, K., *Anniversary Volume Dedicated to M. Chikashige* (*Kyoto Imp. Univ.*) 299 (1930); *Chem. Abs.*, **25**, 2921 (1931).

[34] Lewis, B., and Rideal, E. K., *J. Am. Chem. Soc.*, **48**, 2553 (1926).

[35] Almost no work has been reported on the combination of hydrogen and fluorine. See, however, Bodenstein, M., and Jockersch, H., *Z. anorg. Chem.*, **231**, 24 (1937).

[36] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 889 (1913); *J. Chem. Soc.*, **104** (II), 369 (1913).

[37] Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 722 (1916); *Chem. Abs.*, **11**, 749 (1917).

sides of the equilibrium in vessels of quartz, Uviol glass and Jena glass. These glasses roughly delimited three spectral ranges. The percentage decomposition of each acid at equilibrium is listed in Table 19.

The reactions of hydrogen bromide are very well adapted for the presentation of the method devised by Bodenstein for the treatment of the kinetics of photochemical reactions in general and will be discussed in detail as representative of the methods employed in studying photochemical mechanisms. The case of hydrogen chloride is so complicated that a separate chapter is devoted to its consideration. Before proceeding to a consideration of kinetics, the essential data on the absorption spectra of bromine vapor and hydrogen bromide will be presented.

Absorption of Bromine. In the visible range there is absorption from about 6000A to 3500A, the maximum occurring at about 4100A.[38] Bands from about 5700A converge to a limit at 5107A.[39] At shorter wave-lengths the absorption is continuous, implying a dissociation into a normal atom and one in a metastable state with excitation energy of 10.5 kcal.[40] In the ultraviolet region, bromine vapor at higher pressures exhibits a continuous region from 2700A to the limit of observations at 1560A.[41] Brown[42] has found another band region between 7500 and 6400A, the bands of which apparently converge to a limit indicative of dissociation into two normal atoms. (A dissociation energy of 45.2 kcal. corresponds to 6290A.) Other absorption studies were made by Barratt and Stein,[43] Nakamura,[44] and Hays.[45] The excitation of fluorescence within the range 5000-5600A has been studied by Daure.[46] Wave-lengths in the continuous band below 5000A excite no fluorescence.

Absorption by Hydrogen Bromide. Hydrogen bromide absorbs continuously in the shorter ultraviolet.[47] Tingey and Gerke[48] found continuous absorption to begin at a wave-length which varies with the mass of gas studied, approaching 2640A as a limit as the mass of gas is increased. Coehn and Stuckardt had given 2650A. The absorption limit was unaffected by temperature over the range 25° to 400°C. Datta, however, placed the long-wave threshold at 3260A. The formation of free atoms has been established by Bonhoeffer and Farkas.[49] Goodeve and Taylor[50] believe the molecule dissociates into atoms in normal states. Trivedi's spectroscopic value for the dissociation energy is 92 kcal.[51] There have been but few studies of the decomposition of hydrogen bromide but the work of Warburg[52] is so conclusive that it is generally accepted that the primary process, as in the case of hydrogen iodide is one of photodissociation. The quantum yield is 2.08 at 2070A and 2.00 at 2530A.

Combination of Hydrogen and Bromine. At ordinary temperatures, this

[38] Bovis, P., *J. Phys. Radium*, **10**, 267 (1929); Kuhn, H., *Z. Physik*, **39**, 77 (1926).

[39] Brown, W. G., *Phys. Rev.*, **38**, 1179 (1931).

[40] Turner, L. A., *Phys. Rev.*, **27**, 397 (1926).

[41] Cordes, H., and Sponer, H., *Z. Physik*, **63**, 334 (1930).

[42] Brown, W. G., *Phys. Rev.*, **39**, 777 (1932). For the absorption of liquid bromine, see Porret, D., *Proc. Roy. Soc.*, **A162**, 414 (1937).

[43] Barratt, S., and Stein, C. P., *Proc. Roy. Soc.*, **122**, 582 (1929).

[44] Nakamura, G., *Mem. Coll. Sci. Kyoto*, **9**, 335 (1926); *Chem. Abs.*, **21**, 2431 (1927).

[45] Hays, M. B., *J. Frank. Inst.*, **208**, 363 (1929).

[46] Daure, P., *Compt. rend.*, **183**, 31 (1926).

[47] Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 737 (1916); Warburg, E., *Berlin Akad. Ber.*, 314 (1916); 300 (1918); Datta, A. K., *Z. Physik*, **77**, 404 (1932).

[48] Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, **48**, 1844 (1926).

[49] Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **132**, 235 (1928).

[50] Goodeve, C. F., and Taylor, A. W. C., *Proc. Roy. Soc.*, **A152**, 221 (1935).

[51] Trivedi, H., *Proc. Natl. Acad. Sci. India*, **6**, 29 (1936); *Chem. Abs.*, **30**, 4760 (1936).

[52] Warburg, E., *Berlin Akad. Ber.*, 314 (1916); 300 (1918).

reaction occurs to but a very slight extent, Pusch[53] finding that the absorption of a thousand quanta produces only one molecule of hydrogen bromide. At temperatures of 100° to 200°C., Kastle and Beatty[54] found a reaction to occur. At still higher temperatures (200-300°C.) a thermal reaction occurs in the dark. The kinetics of the dark reaction have been studied by Bodenstein and Lind.[55] Interpretation of this reaction given by Christiansen,[56] Polanyi[57] and Herzfeld[58] involved the thermal dissociation of bromine into atoms.[59]

From the absorption data, it is evident that the photoreaction also proceeds by a mechanism involving free bromine atoms. That the quantum yield exceeds two only at high pressures of hydrogen and that the hydrogen-bromine mixture is insensitive to light at ordinary temperatures are explained on the basis that the reaction

$$Br + H_2 \longrightarrow HBr + H$$

is endothermic. The necessary activation energy can be supplied only thermally at high temperatures.[60]

Bodenstein and Lütkemeyer[61] studied the reaction rate spectrophotometrically by measuring the disappearance of the bromine. They employed temperatures of 160-218°, and irradiated the mixture with moderately intense light from a tungsten arc. The combination takes place with a velocity about 300 times as great as that of the dark reaction at the same temperature. They found also that, under conditions of weak absorption and at the beginning of the reaction, the rate of formation of hydrogen bromide was proportional to the concentration of hydrogen and to the square root of the bromine concentration and the square root of the absorbed energy. When absorption is complete, and in later stages of the reaction when a stationary concentration of bromine atoms has been reached, the rate of the reaction is expressed by

$$\frac{d(HBr)}{dt} = \frac{2k_2(H_2)\sqrt{\frac{\text{No. of quanta absorbed}}{k_5}}}{1 + \frac{k_4(HBr)}{k_3(Br_2)}}$$

The various k values employed refer to the rate constants in the numbered equations which can be set down for the primary process and for the reactions of the products of this reaction with all other substances present. In this case these reactions are

1. $Br_2 + h\nu \longrightarrow 2Br$
2. $Br + H_2 \longrightarrow HBr + H - 16.2$ kcal.
3. $H + Br_2 \longrightarrow HBr + Br + 40.5$
4. $H + HBr \longrightarrow H_2 + Br + 16.2$
5. $Br + Br \longrightarrow Br_2 + 45.2$

[53] Pusch, L., *Z. Elektrochem.*, **24**, 336 (1918).
[54] Kastle, J. H., and Beatty, W. A., *Am. Chem. J.*, **20**, 159 (1898).
[55] Bodenstein, M., and Lind, S. C., *Z. physik. Chem.*, **57**, 168 (1906).
[56] Christiansen, J. A., *Kgl. Danske Videnskab Selskab, Math-fys. Medd.*, **1**, 14 (1919); *Chem. Abs.*, **14**, 1085 (1920).
[57] Polanyi, M., *Z. Elektrochem.*, **26**, 50 (1920).
[58] Herzfeld, K. F., *Z. Elektrochem.*, **25**, 301 (1919); *Ann. Physik*, **59**, 635 (1919).
[59] See, however, Skrabal, A., *Ann. Physik*, **82**, 138 (1927).
[60] Lewis, B., and Rideal, E. K., *J. Am. Chem. Soc.*, **48**, 2553 (1926). Compare the analogous chlorine reactions in the next chapter.
[61] Bodenstein, M., and Lütkemeyer, H., *Z. physik. Chem.*, **114**, 208 (1924).

The plausibility of each of the secondary reactions is then considered. Exothermic reactions are always admitted, although in the case of certain recombinations of free atoms the reaction is not possible except as a result of three-body collisions involving a foreign inert gas or a wall reaction. Endothermic reactions are excluded or admitted, depending upon the possibility of securing the necessary activation energy thermally in a reasonable fraction of collisions at the temperature of the reactants.

The intermediate products are considered to exist (except at the beginning of the irradiation period) in stationary concentrations, reactions leading to their removal summing up to a removal rate equal to the sum of the rates of the reactions by which they are formed. Thus, in this case,

$$\frac{d(Br)}{dt} = 2k_1(Br_2) + k_3(H)(Br_2) + k_4(H)(HBr)$$
$$= \frac{-d(Br)}{dt} = k_2(Br)(H_2) + 2k_5(Br^2)$$

Similarly, for the stationary concentration of H atoms,

$$k_2(H)(Br_2) = k_4(H)(HBr) + k_2(Br)(H_2).$$

Solution of these simultaneous equations makes it possible to express the stationary concentrations of the bromine atoms and of hydrogen atoms in terms of rate constants and the concentrations of hydrogen, bromine and hydrogen bromide molecules. Thus, by subtracting the second from the first equation and solving for (Br), the value k_1/k_5 (Br_2) is obtained. Solving the second equation alone gives for the hydrogen atom concentration

$$\frac{k_2(Br)(H_2)}{k_3(Br_2) + k_4(HBr)}$$

and by substituting in this the value just found for the bromine atom concentration, the stationary H atom concentration becomes

$$[H] = \frac{k_2(H_2)\sqrt{\frac{k_1}{k_5}(Br_2)}}{k_3(Br_2) + k_4(HBr)}$$

The secondary reactions leading to the formation of hydrogen bromide are next summed up and those leading to its destruction deducted.

$$\frac{d(HBr)}{dt} = k_2(Br)(H_2) + k_3(H)(Br_2) - k_4(H)(HBr)$$

By substituting the calculated values for the stationary states of hydrogen and bromine atoms and simplifying algebraically, it is then possible to arrive at an equation which will express the overall kinetics of the reaction. In this case the equation is

$$\frac{d(HBr)}{dt} = \frac{2k_2(H_2)\sqrt{\frac{k_1}{k_5}(Br_2)}}{1 + \frac{k_4(HBr)}{k_3(Br_2)}}$$

In deriving this expression the formation of bromine atoms was assumed to occur thermally. When formation occurs by the absorption of light as in equation (1), the stationary concentration of bromine atoms is given by $(Br) = \sqrt{\frac{n}{k_5}}$, in which n is the number of quanta absorbed per second. In the final equation the radical $\sqrt{\frac{k_1}{k_5}(Br_2)}$ must be replaced by $\sqrt{\frac{n}{k_5}}$. The final result agrees with the observations of Bodenstein and Lütkemeyer that the rate is proportional to the square root of the light intensity at complete absorption. In this expression, it is implied that at the start of the reaction, before hydrogen bromide has formed to an appreciable extent, the denominator becomes unity and the rate is proportional to the hydrogen concentration and the square root of the light intensity. This was observed. Furthermore, if not all of the light is absorbed, the rate also is proportional to the square root of the concentration of the absorbing component, bromine. This also was observed. An examination of the derivation of the rate equation reveals why it is that in reactions involving the dissociation of a molecule by light, the square root of the intensity (or of the absorbing component concentration) so frequently enters the rate expression. It may be noted that in the case of this reaction the derivation was made on the basis of a mechanism for the dark reaction, which was found to give agreement with the expression for the kinetic data of Bodenstein and Lind for the thermal reaction;[62] the necessary modification to make the equation express the photochemical reaction was made subsequently by Bodenstein and Lütkemeyer. The effect of hydrogen bromide in retarding the reaction, as indicated in the denominator, is due to its ability to remove hydrogen atoms by reaction (4). The greater speed of the photochemical reaction is due to the greater stationary concentration of bromine atoms produced by light as compared to those produced thermally at the same temperature (in the range studied). The temperature coefficient of the photoreaction was found to be 1.5 and that of the dark reaction 2.0. From the similarity of mechanisms it was found possible to calculate either temperature coefficient from the other. The value of this coefficient for the photoreaction is due to reaction (3); the temperature coefficient of the dark reaction involves also the thermal dissociation of bromine molecules. The value of 1.5 for the light reaction indicated an activation energy of 17.6 kcal.

The second term in the denominator of either the photo- or thermal reaction rate equation involves a ratio of k_4/k_3. In the thermal reaction this is about 1/10 and independent of temperature. Bodenstein and Jung[63] found the ratio 1/8.4 for experiments both in strong light at room temperature and at 302° in darkness. This independence of the ratio over a wide temperature range indicated that reactions (3) and (4) require no activation energy. The heat of a reaction is the difference between the activation energies of the forward and reverse reactions. As (4) is the reverse of (2) and as (4) has a zero activation energy, the activation energy found for (2) from the temperature coefficient of the light reaction must also be the heat of reaction (2). Using this value, Bodenstein and Jung combined it with the heats of certain other known reactions in order to calculate a value for the heat of dissociation of hydrogen of 107 kcal. This has subsequently been corrected by the use of a better value for one of the reactions they use, to give 103.6 kcal, which is in good agreement with the spectroscopic value 101.9 kcal.

[62] Bodenstein, M., and Lind, S. C., *Z. physik. Chem.*, **57**, 168 (1906).
[63] Bodenstein, M., and Jung, G., *Z. physik. Chem.*, **121**, 127 (1926).

Still other information was derived by Bodenstein and Lütkemeyer from their data. Division of the photo rate equation by the dark rate equation gives for the quotient of the observed rates

$$\frac{I_0}{k_6} \Big/ \frac{k_1(Br_2)}{k_5}$$

The ratio k_1/k_5 was known from the work of Bodenstein and Cramer[64] on the thermal equilibrium constant for the dissociation of bromine. It was therefore possible to calculate k_5. They found in this way that only about one in 800 of the collisions between bromine atoms leads to the formation of molecules. Furthermore this figure appeared to be independent of the temperature and total pressure. Briers and Chapman[65] calculated the mean life of the bromine atoms to be 0.063 second. That the removal rate of bromine atoms should be independent of pressure was unexpected in view of the necessity of three-body collisions for recombination and led Jost and Jung[66] to a study of the effect of variation of total pressure over a wide range on the concentration of bromine atoms and therefore also upon the rate of the reaction. The result was the finding that the reaction velocity is inversely proportional to the square root of the total pressure. An explanation of the apparent discrepancy between these results and those of Bodenstein and Lütkemeyer was given by Bodenstein, Jost and Jung.[67] They pointed out that at low pressures the effects of diffusion of the bromine atoms to the walls where recombination could occur had to be taken into account. At low pressures and weak light intensities (*i.e.*, low concentration of bromine atoms) the rate of formation of hydrogen bromide was found to be proportional to the light intensity rather than to its square root. Jost[68] also found that the formation of hydrogen bromide can be brought about by light of wave-lengths greater than 5107A, and therefore in the banded region of the absorption spectrum of bromine. Here the excited bromine molecules yield bromine atoms on collision with other molecules. The bromine atoms recombine in triple collisions and may also be destroyed on the walls, so that the latter have a characteristic effect on the reaction velocity. The activated bromine atoms formed in the primary reaction affect the reaction velocity in the same manner as unactivated ones because they suffer deactivation before they can react. The velocity constants of the single reactions involved in the formation of hydrogen bromide were recalculated from these data and found in agreement with theory.

Ritchie[69] studied the effect of inert gases on the removal of bromine atoms as affecting the rate of the hydrogen bromide formation at 200°C., the results applying either to the thermal or the light reaction. Under conditions favoring the removal of the atoms to the wall, acceleration of the reaction was produced by foreign gases in the order $CCl_4 > CO_2 > N_2$ and $O_2 > A > H_2$ and He. When the removal was primarily by triple collisions in the gas phase, the efficiency was in the order $CO_2 > O_2 > N_2 > A > He > H_2$. Rabinowitsch and Lehmann[70] find

[64] Bodenstein, M., and Cramer, F., *Z. Elektrochem.*, **22**, 327 (1916).
[65] Briers, F., and Chapman, D. L., *J. Chem. Soc.*, 1802 (1928).
[66] Jost, W., and Jung, G., *Z. physik. Chem.*, **3B**, 83 (1929).
[67] Bodenstein, M., Jost, W., and Jung, G., *J. Chem. Soc.*, 1153 (1929).
[68] Jost, W., *Z. physik. Chem.*, **134**, 92 (1928).
[69] Ritchie, M., *Proc. Roy. Soc.*, **146A**, 828 (1934); Hilferding, K., and Steiner, W., *Z. physik. Chem.*, **B30**, 399 (1935).
[70] Rabinowitsch, E., and Lehmann, H. L., *Trans. Faraday Soc.*, **31**, 689 (1935).

the velocity of homogeneous recombination in the presence of helium to vary inversely with the square root of pressure in accordance with the three-body mechanism, and not according to a conceivable mechanism involving the bromine molecule. At atmospheric pressure, about one double collision in 1300 leads to recombination; this is of the order of the total number of triple collisions expected. Argon and nitrogen are more effective than helium in promoting recombination of bromine atoms.[71]

Armour and Ludlam[72] state that in a streaming mixture of hydrogen and bromine vapor irradiated by the 1850A line of an aluminum spark less than 1 per cent (by weight) of the bromine enters into combination. This was unaltered by a ten-fold variation of the intensity.

It may be noted that Lewis and Rideal believed the reaction to be inhibited by extreme drying. Bodenstein and Jost[73] however, consider this to be unproved; they attribute the results to possible reaction between the hydrogen bromide and the drying agent employed.

The reaction of hydrogen and bromine has been discussed in considerable detail to show the applicability of the concept of stationary states to the formulation[74] of rate expressions from assumed mechanisms and also to illustrate the manner in which photochemical data may be employed as aids to the solution of other physical chemical problems, as for example, the heat of dissociation of hydrogen or the rates of recombination of bromine atoms. In this way the manner in which photochemical investigations interlock with other phases of physical chemistry becomes apparent.

Reactions of Interhalogen Compounds

Mellor and Iredale[75] find hydrogen and iodine chloride to react rapidly in strong light if the hydrogen pressure is large compared with that of the iodine chloride, indicating that this condition favors the reaction $H_2 + Cl \rightarrow HCl + H$ so that excited chlorine atoms may not be required for reaction. In thin glass bulbs a reaction between hydrogen and iodine chloride occurs very slowly in artificial light, more rapidly in diffuse daylight and very rapidly in direct sunlight. The products are chiefly iodine and hydrogen chloride. They later state that the reaction can be brought about with pressures of hydrogen comparable with that of the iodine chloride.[76] Methane also reacts rapidly with iodine chloride in light.[77]

[71] See also Urmston, J., and Badger, R. M., *J. Am. Chem. Soc.*, **56**, 343 (1934).

[72] Armour, R. W., and Ludlam, E. B., *Proc. Roy. Soc. Edinburgh*, **49**, 91 (1929); *Chem. Abs.*, **23**, 3856 (1929).

[73] Bodenstein, M., and Jost, W., *J. Am. Chem. Soc.*, **49**, 1416 (1927).

[74] For a discussion of the validity of the method, see Bodenstein, M., *Trans. Faraday Soc.*, **27**, 409 (1931).

[75] Mellor, D. P., and Iredale, T., *Nature*, **127**, 93 (1931).

[76] *Cf.* Rollefson, G. K., and Lindquist, F. E., *J. Am. Chem. Soc.*, **53**, 1184 (1931).

[77] Ashley, S., and West, W., *Nature*, **127**, 308 (1931).

Chapter 18

The Hydrogen-Chlorine Combination

Although apparently one of the simplest photochemical changes, this reaction has been for over a century the subject of an extraordinary amount of investigation because actually it has offered extreme difficulties in both experimental observation and in interpretation. The experimental results have frequently been in disagreement, largely because small quantities of impurities exert such a remarkable effect upon the reaction that reproducible results are difficult to secure. Oxygen, which can be removed from chlorine only with great difficulty, has an inhibiting effect, difficult to eliminate. Other impurities, entirely unsuspected, have been responsible for an inert period after the start of illumination before the reaction begins to build up to its maximum rate. Since studies on this reaction were among the first quantitative photochemical investigations, the finding of this induction period was for a time assumed to be a general photochemical phenomenon, an error which greatly affected the early development of photochemical theory. A thorough review of the history of this reaction would fill many pages. Since excellent summaries are available[1] and since most of the data are concerned with the effects of visible rather than ultraviolet light, the account in this chapter will be limited to a consideration of certain of the more significant features of the work on the reaction, following a statement of the viewpoint at present most generally held in regard to the mechanism.

Spectral Absorption Data

1. **Hydrogen Chloride.** The absorption of hydrogen chloride consists only of four continuous bands in the short-wave region (2150-1850, 1750-1650, 1580-1290 and 1270-1240A). The absorption spectra of the halide apparently has no significance for the course of the reaction involving hydrogen and chlorine.[2] When irradiated in its absorption region, hydrogen chloride dissociates into a normal hydrogen and an excited chlorine atom, Trivedi[3] finding from the absorption spectrum a heat of dissociation equivalent to 103.9 kcal. Coehn and Wassiljewa[4] and Berthelot and Gaudechon[5] observed slight decomposition to occur as a result of irradiating hydrogen chloride in this wave-length region. According to Schultz[6] not more than 5 molecules may be decomposed per quantum absorbed.

2. **Absorption of Chlorine.** Chlorine absorbs in two broad regions. The first, to which the gas owes its color, extends from about 6430A (or possibly

[1] Griffith, R. O., and McKeown, A., "Photo-Processes in Gaseous and Liquid Systems," London, Longmans, Green and Co., 1929, Chapter X; Bodenstein, M., *Trans. Faraday Soc.*, **27**, 413 (1931); Thon, N., *Fortschritt Chem. Physik, physik. Chem.*, **18**, No. 11 (1926); Marshall, A. L., *Trans. Am. Electrochem. Soc.*, **49**, 143 (1926).

[2] Leifson, S., *Astrophys. J.*, **63**, 73 (1926).

[3] Trivedi, H., *Proc. Natl. Acad. Sci. India*, **6**, 18 (1936); *Chem. Abs.*, **30**, 4759 (1936).

[4] Coehn, A., and Wassiljewa, A., *Ber.*, **42**, 3183 (1909).

[5] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 889 (1913).

[6] Schultz, C. T., *J. chim. phys.*, **26**, 506 (1929); *Brit. Chem. Abs.* **A**, 173 (1930).

longer) to about 2500A. Its maximum lies at about 3340A. Extinction values have been given by v. Halban and Siedentopf.[7] There is a minimum in the yellow and the absorption then increases toward longer wave-lengths to a maximum which probably lies between 6140 and 6430A. The spectrum at longer wave-lengths is banded, the absorption coefficients of the bands having very low values.[8] The edges of the bands converge to a limit at 4785A, the absorption being continuous at shorter wave-lengths.[9] It is only in the continuous region that the absorption coefficients attain large values. Here the molecule is dissociated into one normal chlorine atom and one bearing an energy of excitation of 0.109 volt.[10] Since the maximum absorption occurs at a wave-length much shorter than the convergence limit, the excess energy of the light must appear as large amounts of kinetic energy possessed by the dissociated atoms.

The second absorption region extends from about 1900 to 1560A and is entirely continuous.[11] It corresponds to a dissociation similar to that produced by absorption in the region of longer wave-lengths, except that the atoms produced are endowed with greater kinetic energies. From these considerations it is evident that the primary process in the hydrogen-chlorine combination must consist in the formation of chlorine atoms when the mixture of gases is irradiated with wave-lengths shorter than 4785A.

To account for various features of the photochemical reaction anomalies of absorption have been assumed. Statements that the absorption by chlorine is dependent upon the intensity of the incident light[12] could not be confirmed by Gray and Style.[13] For a long period water was believed necessary for the photochemical reaction between hydrogen and chlorine. It was stated that the disposition of energy absorbed by moist and by dry samples of chlorine is different.[14] No difference in absorption was observed by v. Halban and Siedentopf, Kistiakowsky[15] or Kornfeld and Steiner.[16] Furthermore, no fluorescence could be detected within the continuous region.

Budde Effect. A phenomenon which excited considerable interest and which at one time appeared important for the explanation of the mechanism of the hydrogen-chlorine combination was the observation by Budde[17] that chlorine gas expands when illuminated by white or blue light but not when red or yellow light is employed. He found the expansion the result of a temperature increase, an observation confirmed by Bevan.[18] Richardson[19] found the expansion to be roughly proportional to the intensity of the light employed. The effect is usually attributed to heat liberated as a result of the recombination of chlorine atoms formed by the absorption within the continuous region. The effects of small amounts of moisture on the extent of this effect have been discussed since the observations of Shenstone,[20] who found pure dry chlorine to give only a very small Budde effect. This effect could be increased by the admission of some moisture.[21]

[7] v. Halban, H., and Siedentopf, K., *Z. physik. Chem.*, **103,** 71 (1922).
[8] Kuhn, H., *Z. Physik,* **39,** 77 (1926).
[9] Elliott, A., *Proc. Roy. Soc.* **123,** 629 (1929); **127,** 638 (1930).
[10] Birge, R. T., *Phys. Rev.,* **35,** 133 (1930).
[11] Cordes, H., and Sponer, H., *Z. Physik,* **63,** 334 (1930).
[12] Weigert, F., and Brodmann, L., *Z. physik. Chem.,* **106,** 426 (1923).
[13] Gray, L. T. M., and Style, D. W. G., *Proc. Roy. Soc.* **126A,** 603 (1930).
[14] Mellor, J. W., *J. Chem. Soc.,* **81,** 1280 (1902).
[15] Kistiakowsky, G. B., *J. Am. Chem. Soc.,* **49,** 2194 (1927).
[16] Kornfeld, G., and Steiner, W., *Z. Physik,* **45,** 325 (1927).
[17] Budde, E., *J. prakt. Chem.,* **7,** 376 (1873).
[18] Bevan, P. V., *Phil. Trans.,* **202,** 90 (1904).
[19] Richardson, A., *Phil. Mag.,* **32,** 221, 277 (1891).
[20] Shenstone, W. A., *J. Chem. Soc.,* **71,** 471 (1897).
[21] See also Ludlam, E. B., *Proc. Roy. Soc. Edinburgh,* **34,** 197 (1924).

Kistiakowsky[22] attributed the water dependence of the effect to the necessity for inert molecules to carry off the energy of recombination of chlorine in three-body collisions. In the absence of water, the free chlorine atoms could combine only on the glass walls of the vessel. The large heat capacity and relatively good heat conductance of the vessel would, however, prevent the heating of the gas and so the Budde effect would be missed. On the other hand, Martin, Cole and Lent[23] and more recently, Kiastiakowsky[24] have denied the effect of drying in lessening the photoexpansion of chlorine. Narayana,[25] however, states that the Budde effect cannot be observed in dry gases, unless the vessel is carefully vacuum-insulated. In accordance with the theory that a primary dissociation is essential, the effect is absent in chlorine illuminated by wave-lengths greater than 5000A and in bromine above 5500A. It varies as the pressure of the halogen and as the square root of the intensity of the light.

In the case of bromine, Lewis and Rideal[26] have advanced evidence in support of a different mechanism. They believed a bromine-hydrate (heat of formation 1.09 kcal.) to be dissociable by wave-lengths 5700-5400A, in the band rather than in the dissociation region of the spectrum. Thus the bromine hydrate could be dissociated by wave-lengths longer than those required for the dissociation of dry bromine. Recombination of the bromine and water was held to give rise to the heat which produces the characteristic expansion. Matthews[27] has found drying to lessen somewhat the Budde effect, although it could not be entirely eliminated in this manner.

Mechanism of the Hydrogen-Chlorine Combination

The outstanding characteristic of the hydrogen-chlorine combination is the high quantum yield. Bodenstein[28] calculated that, were it possible to eliminate traces of inhibiting oxygen from the chlorine employed, the yield should be approximately 10^6. Kornfeld and Müller[29] found it to be 1.10×10^5 for light of 4360A. Harris[30] has, by using blue light and very carefully purified gases, obtained a value of 6×10^5 and Bodenstein and Winter[31] of 4.2×10^6 in silver vessels. This corresponds to an average chain duration of 16 seconds. Obviously, such quantum yields require a chain mechanism and many have been proposed. At this point, mention of the mechanism which apparently is most favored, will be made and discussion of the effects of inhibitors will be postponed until the experimental data have been discussed. The primary process is a photodissociation of the chlorine into atoms. The subsequent reactions which form the chain were first suggested by Nernst.[32]

$$(1)\quad Cl_2 + h\nu\,(< 4785\text{A}) \longrightarrow Cl + Cl$$
$$(2)\quad Cl + H_2 \longrightarrow HCl + H$$
$$(3)\quad H + Cl_2 \longrightarrow HCl + Cl$$

Rodebush and Klingelhöfer[33] have advanced more cogent evidence than that originally suggested by Nernst for the thermodynamic possibility of reaction (2), although they believe that only every 10^5th collision leads to reaction. The acti-

[22] Kistiakowsky, G. B., *J. Am. Chem. Soc.,* **49,** 2199 (1927).
[23] Martin, W. H., Cole, A. F. W., and Lent, E. E., *J. Phys. Chem.,* **33,** 148 (1929).
[24] Kistiakowsky, G. B., *J. Am. Chem. Soc.,* **51,** 1395 (1929).
[25] Narayana, T. S., *Indian J. Physics,* **9,** 91 (1934); *Chem. Abs.,* **29,** 684 (1935).
[26] Lewis, B., and Rideal, E. K., *J. Chem. Soc.,* 583, 596 (1926).
[27] Matthews, E., *Trans. Faraday Soc.* **25,** 41 (1929); *cf.* Ritchie, M., and Ludlam, E. B., *J. Chem. Soc.,* 1680 (1937).
[28] Bodenstein, M., *Z. physik. Chem.,* **85,** 351 (1913).
[29] Kornfeld, G., and Müller, H., *Z. physik. Chem.,* **117,** 242 (1925).
[30] Harris, L., *Proc. Nat. Acad. Sci.,* **14,** 110 (1928).
[31] Bodenstein, M., and Winter, E., *Sitzber. preuss. Akad. Wiss., Physik-math. Kl.* 2 (1936).
[32] Nernst, W., *Z. Elektrochem.,* **24,** 335 (1918).
[33] Rodebush, W. H., and Klingelhöfer, W. C., Jr., *Proc. Nat. Acad. Sci.,* **18,** 531 (1932); *J. Am. Chem. Soc.,* **55,** 130 (1933).
[34] Marshall, A. L., *J. Phys. Chem.,* **29,** 842 (1925).

vation energy is 6.1 kcal. Marshall[34] calculated for reaction (2) a free energy change of approximately zero. Reaction (3) is believed by Bodenstein to occur at each hundredth collision. Since it regenerates a free chlorine atom, the chain mechanism would be readily apparent did reaction (2) occur.

Many efforts were made to demonstrate experimentally the occurrence of reaction (2), including the work of Jost and Schweitzer.[35] Could this reaction be admitted, it is apparent that the great difference between the hydrogen-bromine and the hydrogen-chlorine combinations would be readily explicable. The failure of many direct attempts to show experimental proof for reaction (2), however, delayed for several years the acceptance of the simple Nernst chain mechanism and led to the proposal of a number of alternative mechanisms which attempted to avoid the use of this reaction. Included among these proposals were the presence of excited chlorine molecule chains or of chains carried by excited HCl or by a postulated triatomic chlorine molecule.

Attempts to activate chlorine by a brush electric discharge or by a mercury lamp so that when conducted into unilluminated hydrogen the two substances would produce hydrogen chloride were made (unsuccessfully) by Wendt.[36] Other unsuccessful attempts were described by Bodenstein and Taylor[37] and by Marshall.[38] Jost and Schweitzer were able to demonstrate the reaction (2) by passing a very rapid stream of irradiated chlorine into hydrogen. The free atoms, however, recombine rapidly on the walls of the conducting tube and the experiment fails when the irradiated gas remains in the tube longer than 10^{-4} second. Nevertheless, with the demonstration of the possibility of the reaction, the Nernst chain becomes admissible. It is thus conceivable that there can be a long-continued interplay of reactions (2) and (3) leading to the production of large numbers of molecules of hydrogen chloride consequent upon the absorption of one quantum of light, before the free atoms which carry the chains are lost by wall reactions or by interactions with impurities, *e.g.*, oxygen.

History of the Work on the Reaction. That a mixture of hydrogen and chlorine explodes in bright sunlight and reacts slowly in diffused light was first observed by Cruikshank.[39] Quantitative rate measurements, the first on any photochemical change, were made by Draper[40] by means of a "tithonometer." In this apparatus the hydrogen chloride produced was absorbed in water, and the volume contraction was followed by the movement of a column of liquid along a capillary. Draper found indigo rays the most powerful in causing the contraction, as did Favre and Silbermann.[41]

In the course of this work what has come to be known as the Draper effect[42] was discovered. This consists of a brief expansion on exposure to light, followed by a period in which there is no pressure change, and then by a contraction. The details of the Draper effect were studied by Mellor and Anderson,[43] Bevan,[44] and by Weigert and Kellerman.[45] Bevan, who could produce the Draper effect only by use of fairly intense light, attributed the effect to a rise of temperature accompanying the formation of

[35] Jost, W., and Schweitzer, H., *Z. physik. Chem.*, **13B,** 373 (1931).

[36] Wendt, G. L., *Chem. Met. Eng.*, **24,** 83 (1921); Wendt, G. L., Landauer, R. S., and Ewing, W. W., *J. Am. Chem. Soc.*, **44,** 2377 (1922). See, however, Venkataramaiah, Y., *J. Phys. Chem.*, **27,** 74 (1923).

[37] Bodenstein, M., and Taylor, H. S., *Z. Elektrochem.*, **22,** 202 (1916).

[38] Marshall, A. L., *J. Phys. Chem.*, **30,** 757 (1926).

[39] Cruikshank, W., *Nicholson's J.*, **5,** 202 (1801).

[40] Draper, J., *Phil. Mag.*, **19,** 195 (1841); **23,** 40 (1843); **25,** 237 (1844).

[41] Favre, P. A., and Silbermann, J. T., *Ann. chim. phys.*, **37,** 497 (1853). Allmand, A. J., and Beesley, E. [*J. Chem. Soc.*, 2694, 2709 (**1930**); 157 (**1934**)] find the violet region the most effective.

[42] Draper, J., *Phil. Mag.*, **26,** 476 (1845).

[43] Mellor, J. W., and Anderson, W. R., *J. Chem. Soc.*, **81,** 414 (1902).

[44] Bevan, P. V., *Phil. Trans.*, **202,** 81 (1904).

[45] Weigert, F., and Kellerman, K., *Z. physik. Chem.*, **107,** 1 (1924).

hydrogen chloride. Weigert made a detailed study of the time relations involved, employing a photographic Töpler cloud method depending upon local changes of refractive index. The magnitude of the effect was related to the degree of drying of the gases. The cloud observed when a mixture of chlorine and electrolytic gas was irradiated with light of short wave-length paralleled the Draper effect in time-intensity relations. The cloud was assumed due to a warming of the gas and the amount of thermal expansion corresponded with the calculated amount of heat which is liberated during the production of the hydrogen chloride. Weigert's theory of clustering about a group of two molecules between which an electron has passed from the hydrogen molecule to the chlorine molecule did not prove significant. His experimental observation that the change in density did not begin until 10^{-4} second after irradiation by a single spark discharge and attained its maximum only some hundredths of a second after the irradiation gave direct evidence for the existence of a chain reaction.

Induction Period. Bunsen and Roscoe made studies of the rate of the reaction; an improved "actinometer" was used for correlating the reaction rate and the light intensity.[46] In the course of this work they described in detail an earlier observed induction period to which they ascribed unwarranted *general* photochemical significance. The details given by them and by later workers[47] were confusing and indicated the induction period to be dependent on the length of the gas column irradiated, the intensity of the light, the temperature and the previous history of the gas. The interpretation of the results was further complicated by the belief of Bunsen and Roscoe that the absorption of the gases during reaction is increased over that of unreacting gases, a view now known to have been erroneous. The simple explanation that the induction period is due to the presence of small amounts of inhibiting impurities which are destroyed in large part during the inert period was established by Burgess and Chapman.[48] They found no difference in the extinction of irradiated and non-irradiated gas mixtures. Also, oxygen did not affect the length of the induction period, and traces of ammonia could produce very long induction periods, the duration of which varied directly as the concentration of the added ammonia. A later suggestion by Chapman and McMahon[49] that the inhibition should be attributed to the production of NCl_3 by the interaction of chlorine with the ammonia was, however, considered untenable by Norrish.[50] Norrish advanced the view that the ammonia derived from the impurities was adsorbed on the surface of the vessel, poisoning the latter for certain surface reactions involving a water-chlorine compound. Arguments were raised against this theory by Cathala.[51] Griffiths and Norrish[52] have accepted the view that the induction period is due to the formation of NCl_3, which undergoes photosensitized decomposition in the presence of excess chlorine by short reaction chains. The quantum efficiency of this reaction falls to about two as the chlorine pressure is increased.

Nitric oxide (but not nitrous oxide) and chlorine dioxide also inhibit the reaction.[53] Oxygen apparently slows the rate of the reaction rather than causes an induction period. The effect of oxygen in inhibiting the reaction is not attended by its total disappearance, as is that of the inhibitors responsible for the

[46] Bunsen, R., and Roscoe, H., *Pogg. Ann.*, **96,** 373 (1855); **100,** 193, 483 (1857); **101,** 32, 237, 275 (1857); **108,** 193 (1859); **117,** 531 (1862); Reprinted in *Ostwald's Klassiker,* No. 34 and 38 (**1892**).

[47] Pringsheim, E., *Wied. Ann.*, **32,** 384 (1887); Mellor, J. W., *J. Chem. Soc.*, **81,** 1292 (1902).

[48] Burgess, C. H., and Chapman, D. L., *J. Chem. Soc.*, **89,** 1399 (1906).

[49] Chapman, D. L., and McMahon, P. S., *J. Chem. Soc.*, **95,** 1717 (1909); **97,** 847 (1910).

[50] Norrish, R. G. W., *J. Chem. Soc.*, **127,** 2316 (1925).

[51] Cathala, J., *Bull. Soc. Chim.*, **39,** 612 (1926).

[52] Griffiths, J. G. A., and Norrish, R. G. W., *Trans. Faraday Soc.*, **27,** 451 (1931); *Proc. Roy. Soc.*, **147A,** 140 (1934).

[53] Chapman, D. L., and McMahon, P. S., *J. Chem. Soc.*, **95,** 959 (1909).

induction period. The rate of the formation of hydrogen chloride has been found to be inversely proportional to the oxygen concentration, at least over the range, 0.09 to 1.00 per cent.[54]

Effects of Water Vapor. From the earliest to the most recent studies, attention has been directed to the effects of traces of water vapor on the hydrogen-chlorine combination. Baker[55] claimed that under conditions of extreme dryness, the reaction proceeds only very slowly in direct sunlight, but Mellor and Russell[56] found that even these extremely dry mixtures could be made to explode by an electric spark. Bodenstein and Dux[57] found the rate of combination of the gases to be unaffected by drying down to a water vapor pressure of 10^{-3} mm. of mercury. Tramm,[58] however, found that drying by a special liquid air technique prevented the combination from occurring in sunlight. Coehn and Jung[59] claimed that the photochemical reaction was prevented when the water vapor pressure was reduced below 10^{-7} mm. and visible light was the source employed. When the effective light was of wave-length shorter than about 2540A the reaction was not prevented by drying, although the quantum yield was lowered to about eight. On the basis of these results, Norrish[60] advanced the theory that water is required as a catalyst in the primary process. He believed an intermediate compound $\begin{matrix} H \\ H \end{matrix}\!>\!O\!<\!\begin{matrix} Cl \\ Cl \end{matrix}$ to be formed and adsorbed on the walls of the vessel where subsequent reaction occurs. Coehn's explanation of the effect of water (an effect due to water in atomic chlorine reactions) appeared inadequate both to Norrish and to Cathala.[61] The latter worker, however,[62] was unable to accept the theory of Norrish. Kistiakowsky,[63] pointed out that the theory of Norrish had been disproved by the experiments of Coehn and Heymer[64] in which a chlorine and hydrogen mixture reacted on exposure to radiation in apparatus arranged to minimize solid and liquid surfaces. For a time it was believed that water might be required to enable the absorption of radiation by chlorine leading to dissociation of the latter into atoms.[65]

As the spectroscopic evidence on the dissociation process gained prominence, it became necessary to discard such views. The effect of water vapor was next attributed to some possible influence exerted by it on the rate of recombination of free chlorine atoms.[66] Recently, however, in view of the inadequacy of the explanations which could be advanced to explain the mechanism by which water vapor aids the reaction, the tendency has been to reëxamine the validity of the phenomenon. Particularly is this necessary, since it would be very difficult to explain why water vapor should have a greater effect upon chlorine atoms produced by visible radiations than by shorter rays as had been claimed by Coehn and Tramm. Bodenstein

[54] Bodenstein, M., and Dux, W., *Z. physik. Chem.*, **85**, 297 (1913).
[55] Baker, H. B., *J. Chem. Soc.*, **65**, 612 (1894).
[56] Mellor, J. W., and Russell, E. J., *J. Chem. Soc.*, **81**, 1272 (1902).
[57] Bodenstein, M., and Dux, W., *Z. physik. Chem.*, **85**, 297 (1913).
[58] Tramm, H., *Z. physik. Chem.*, **105**, 356 (1923).
[59] Coehn, A., and Jung, G., *Ber.*, **56**, 696 (1923).
[60] Norrish, R. G. W., *J. Chem. Soc.*, **127**, 2316 (1925); *Trans. Faraday Soc.*, **21**, 575 (1925).
[61] Cathala, J., *Compt. rend.*, **181**, 33 (1925).
[62] Cathala, J., *Bull. Soc. Chim.*, **39**, 612 (1926).
[63] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2194 (1927).
[64] Coehn, A., and Heymer, G., *Naturwiss.*, **14**, 299 (1926); *Ber.*, **59B**, 1794 (1926).
[65] Lewis, B., *Nature*, **120**, 473 (1927); Weigert, F., *Z. physik. Chem.*, **106**, 426 (1923). Ichikawa, T., *Z. physik. Chem.*, **10B**, 299 (1930).
[66] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2194 (1927).

and Bernreuther[67] suggest that the earlier observations may have been due to the accidental introduction of strong inhibitors such as metal chlorides in the drying methods employed. The work of Rollefson and Potts[68] indicates that at low temperatures at least, the presence of water vapor has no marked effect on the rate of the reaction.

Development of Chain Mechanisms. The first chain mechanism suggested by Bodenstein involved an ionized chlorine molecule[69] but this was soon shown to be excluded[70] by the observations that no ionization occurs in irradiated chlorine gas,[71] or during the photocombination of hydrogen and chlorine.[72] Bodenstein[73] next proposed a mechanism in which the chains were assumed to be carried both by activated chlorine and activated hydrogen chloride molecules, a view supported in principle (although not in the details of chain propagation) by Stern and Volmer.[74]

The dissociation theory of Nernst[75] was proposed in 1918; many attempts followed to decide between the "hot molecule" and the dissociation theories. Attempts to compare rates and quantum yields of light and α-ray induced reactions[76] failed to afford a basis for a decision. Much labor was devoted to efforts to settle the question by kinetic studies. The earlier attempts were also equivocal, and it became evident that with sufficient ingenuity the kinetic data obtained under various experimental conditions might be interpreted with some degree of success by employing the concepts of either theory. The details of the many proposed mechanisms, some of which involved as many as eleven reaction constants (for the most part undetermined or undeterminable) cannot be given here.

Reaction Kinetics[76a]

Contrary to Baly and Barker,[77] more recent observers find the rate of the formation of hydrogen chloride proportional to the light intensity.[78] Rollefson found the rate of formation also proportional to the hydrogen and chlorine[79] concentrations. He reasoned that if the reaction were due to excited molecules, the velocity constant should decrease rapidly at low pressures, since the time between collisions would then be long enough to permit the excitation energy to be lost by fluorescence. Should the reaction be due to free atoms, the rate constant should be independent of the pressure. From kinetic considerations and from the probable life of an excited chlorine molecule, he calculated that it should be possible

[67] Bodenstein, M., and Bernreuther, F., *Berl. Preuss. Akad. Wiss., Phys. math. Klasse*, 333 (**1933**); *Chem. Abs.*, **27**, 3669 (1933).
[68] Rollefson, G. K., and Potts, J. C., *J. Am. Chem. Soc.*, **55**, 860 (1933).
[69] Bodenstein, M., *Z. physik. Chem.*, **85**, 329 (1913).
[70] LeBlanc, M., and Volmer, M., *Z. Elektrochem.*, **20**, 494 (1914).
[71] Ludlam, E. B., *Phil. Mag.*, **23**, 757 (1912).
[72] Thomson, J. J., *Proc. Cambr. Phil. Soc.*, **11**, 901 (1901).
[73] Bodenstein, M., *Z. Elektrochem.*, **22**, 53 (1916).
[74] Stern, O., and Volmer, M., *Z. wiss. Phot.*, **19**, 275 (1920).
[75] Nernst, W., *Z. Elektrochem.*, **24**, 335 (1918).
[76] Bodenstein, M., *Z. Elektrochem.*, **22**, 53 (1916); Taylor, H. S., *J. Am. Chem. Soc.*, **37**, 24 (1915); **38**, 280 (1916). Porter, F., Bardwell, D. C., and Lind, S. C., *J. Am. Chem. Soc.*, **48**, 2603 (1926).
[76a] For the evaluation of the various rate constants, see Taylor, H. S., *J. Phys. Chem.*, **42**, 789 1453
[77] Baly, E. C. C., and Barker, W. F., *J. Chem. Soc.*, **119**, 653 (1921).
[78] Chapman, M. C. C., *J. Chem. Soc.*, **125**, 1521 (1924); Marshall, A. L., *J. Phys. Chem.*, **29**, 1453 (1925); Allmand, A. J., and Beesley, E., *J. Chem. Soc.*, 2693 (**1930**). Rollefson, G. K., *J. Am. Chem. Soc.*, **51**, 770 (1929); Bateman, J. B., and Craggs, H. C., *Trans. Faraday Soc.*, **27**, 445 (1931); Bodenstein, M., and Unger, W., *Z. physik. Chem.*, **11B**, 253 (1930); see, however, Squire, G. V. V., and Allmand, A. J., *J. Chem. Soc.*, 1869 (**1937**).
[79] See, however, Bodenstein, M., and Dux, W., *Z. physik. Chem.*, **85**, 297 (1913); Thon, N., *Z. physik. Chem.*, **124**, 327 (1926). For the influence of oxygen on the rate, see Chapman, M. C. C., *loc. cit.*; Norrish, R. G. W., and Rideal, E. K., *J. Chem. Soc.*, **127**, 787 (1925).

to distinguish between these mechanisms at a hydrogen pressure of one millimeter. His data showed no change in the rate constant as the pressure was decreased below this limit and therefore afforded support for the dissociation mechanism.

Recently efforts have been directed toward an understanding of the manner in which, in pure gases, the chains are broken by the removal of the atoms. Reactions at the wall were suggested by Chapman and Grigg [80] for destroying the catalyst (the nature of which then was not considered) since the reaction was slower in capillary tubes than when conducted under the same light intensity in tubes of wider bore. Trifonoff,[81] who suggested that grease on the stopcocks might start the reaction, believed that recombination of atoms diffused to the walls at low pressures might break the chains. At pressures above 30 mm., he believed the processes to occur chiefly in the free space, but below 10 mm. practically all of the chains break down at the surfaces of the walls. Bodenstein and Unger were also of the opinion that at higher pressures the chains must be broken by some compound present in the reaction space. A volatile deposit, possibly of a silicon oxychloride, has been detected on the walls of vessels in which free chlorine atoms had been produced. Hertel [82] thought that this might be responsible for breaking the chains, since the rate of formation of hydrogen chloride could be lowered by carrying out the reaction in vessels in which chlorine had previously been irradiated. He had found that the rate [83] might be expressed by $k_1(H_2)(Cl_2)^2$ when the chlorine is present in great excess and by $k_2(H_2)^2(Cl_2)$ when the hydrogen is in great excess. He also gave a more general equation, which need not be reproduced here. Hertel believed that the observed rate could be accounted for on the assumption that oxygen terminates the chains by combining with the hydrogen atoms. Chapman and Gibbs [84] find the rate of the reaction proportional to the square root of the intensity of the light when the chlorine used has been very carefully freed from oxygen and other inhibiting impurities.

Behavior at very low pressures similar to that found by Rollefson has also been reported by Allmand and Craggs,[85] the reaction proceeding at the normal rate even at chlorine pressures as low as 0.012 mm. Water vapor also failed to affect the rate except at low total pressures. They stated that at total pressures of 2 mm. ultraviolet light affords lower quantum yields than does visible light, but this difference is not observed at higher pressures. It was thought that it might be accounted for by the formation of triatomic chlorine molecules by the ultraviolet of short wave-length. By quantum mechanical considerations, Rollefson and Eyring [86] concluded that, for all the halogens, molecules of the type X_3 are stable at room temperatures with respect to dissociation into X_2 and X. Cremer [87] had previously suggested the possibility that this molecule might function as a chain carrier, as had Cathala [88] who called it "chlorozone." [89]

[80] Chapman, D. L., and Grigg, P. P., *J. Chem. Soc.*, 3233 (1928).

[81] Trifonoff, A., *Z. physik. Chem.*, **3B**, 195 (1929); **6B**, 118 (1929); Trifonoff, A., and Ryabinin, G., *Trans. State Phys.-Tech. Lab. (Moscow)*, No. **14**, 26 (1930); *Chem. Abs.*, **24**, 1297 (1930).

[82] Hertel, E., *Z. physik. Chem.*, **15**, 325 (1932).

[83] Hertel, E., *Z. physik. Chem.*, **14B**, 443 (1931).

[84] Chapman, D. L., and Gibbs, F. B., *Nature*, **127**, 854 (1931).

[85] Allmand, A. J., and Craggs, H. C., *Nature*, **130**, 927 (1932); *J. Chem. Soc.*, 241 (1936); 1889 (1937). Craggs, H. C., Squire, G. V. V., and Allmand, A. J., *J. Chem. Soc.*, 1878 (1937).

[86] Rollefson, G. K., and Eyring, H., *J. Am. Chem. Soc.*, **54**, 170 (1932).

[87] Cremer, E., *Z. physik. Chem.*, **128**, 285 (1927).

[88] Cathala, J., *J. chim. Phys.*, **25**, 182 (1928).

[89] For further discussion of chain carriers for this reaction see Göhring, R., *Z. Elektrochem.*, **27**, 516 (1921); Chapman, D. L., *Trans. Faraday Soc.*, **21**, 547 (1925) and Warburg, E., *Z. Elektrochem.*, **27**, 139 (1921).

[90] Bodenstein, M., and Schenk, P. W., *Z. physik. Chem.*, **20B**, 420 (1933).

Allmand and Craggs state that the presence of 0.1 mm. of oxygen retards the reaction between chlorine and less than 0.01 mm. of hydrogen. It has no effect, however, when there is 0.01 to 0.5 mm. of hydrogen, but under these conditions the oxygen is consumed.

Results of Bodenstein and Schenk [90] on the relative yields of hydrogen chloride and of water in streaming mixtures of chlorine, hydrogen and oxygen at 60°C. have been criticized by Chapman and Watkins,[91] who employed mixtures rich in oxygen. Ritchie and Norrish,[92] who determined the reaction rate by measuring the chlorine absorption, found hydrogen chloride to have a pronounced inhibiting effect on mixtures which contained oxygen. In the absence of oxygen, the quantum efficiency is given by the expression

$$\frac{2.8\times10^3(H_2)(Cl_2)}{(Cl_2)+1.7(HCl)(I_{Abs})^{0.4}}.$$

Their maximum quantum yield was 1.2×10^5. The velocity of hydrogen chloride formation varies with the 0.6 power of the intensity of the absorbed light in approximate agreement with Chapman and Gibbs. Reaction chains are terminated mainly by self-neutralization.[93] In the presence of oxygen, both hydrogen chloride and hydrogen have inhibiting effects, that of the former being four times that of the latter. With increasing hydrogen pressures, the quantum efficiency rises through a maximum. For mixtures rich in oxygen, it varies inversely as the oxygen pressure and is independent of the light intensity. The quantum efficiency is also reduced by inert gases.[94] At low concentrations of oxygen, it shows a dependence on the light intensity.

According to Krauskopf and Rollefson,[95] as the ratio of oxygen to chlorine is increased, the ratio of the production of water to that of hydrogen chloride approaches a limit between one and two. From its temperature dependence, the activation energy for the reactions yielding hydrogen chloride appears to be greater than that for those yielding water. They hold that the existence of the limit for the ratio of the two products shows that the Nernst chains must be terminated by a reaction $H+O_2\rightarrow HO_2$ rather than by $Cl+O_2\rightarrow ClO_2$. Rollefson and Potts [96] state that at temperatures below 172°K., the melting point of chlorine, the rate depends on the square root of the light absorbed. From the temperature coefficients, observed at 3600A, the heat of activation is 5.8 kcal. At low temperatures the value 4.6 kcal. is, however, found. They accept the suggestion that a volatile silicon oxychloride terminates the chains. They suggest further that the large inhibiting effect of hydrogen chloride observed by Norrish and Ritchie may have been due to the introduction of an inhibiting impurity in the hydrogen chloride added. The rate equation given by Rollefson and Potts is said to be valid at temperatures as low as 200°K. The equation is:

$$\frac{d(HCl)}{dt}=kI_{Abs}(H_2)\frac{1}{1+k_1\dfrac{(HCl)}{(Cl_2)}},$$

[91] Chapman, D. L., and Watkins, J. S., *J. Chem. Soc.*, 743 (1933).

[92] Ritchie, M., and Norrish, R. G. W., *Proc. Roy. Soc.*, **140**, 99, 112, 713 (1933).

[93] See also Tamura, M., *Rev. Phys. Chem. Japan*, **11**, 1 (1937); *Chem. Abs.*, **32**, 1184 (1938).

[94] Ritchie, M., *J. Chem. Soc.*, 857 (1937).

[95] Krauskopf, K. B., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 327 (1934); see also Ritchie, M., *J. Chem. Soc.*, 857 (1937).

[96] Rollefson, G. K., and Potts, J. C., *J. Am. Chem. Soc.*, **57**, 1027 (1935).

in which $k_1 \leqq 0.1$. Some of the proposed chain mechanisms have been discussed by Bates.[97] An interesting direct method of demonstrating the existence of a chain reaction has been the application of the para-hydrogen test for the presence of free hydrogen atoms,[98] to which reference has been made in a preceding chapter. Kokochashvili[99] has studied the reaction by the aid of very brief irradiations (.08 second) of high intensity secured by magnesium flashes, and has discussed his results from the standpoint of chain mechanisms. Deuterium molecules are less reactive than hydrogen, the activation energy being slightly higher for the former.[100] Farkas and Farkas[101] find the reaction with deuterium to proceed at one-third the rate of that with hydrogen. They ascribe the difference in rates to the larger zero-point energy of hydrogen as compared with deuterium. The calculated additional activation energy of 0.8 kcal. required by deuterium agrees well with the difference in zero-point energy between H^1_2, HD and D_2 of 810 and 1710 cal.

Thresholds and the Effects of Wave-Lengths

Within the continuous region, Bodenstein and Schenk[102] found the quantum yield to be independent of the wave-length. Allmand and Beesley,[103] using filters, gave the following *relative* values: 2600A, 0.10; 3130A, 0.49; 3650A, 0.53; 4050A, 1.00; 4360A, 0.67 and 5460A, 0.22. On the other hand, Bateman and Allmand[104] found the quantum yield independent of the wave-length between 4000A and 4900A, but observed it to fall slowly on either side of this region. The earlier results were attributed to the accidental use of a glass window. A result at 4920A was considered anomalous since the ratio between the yield at this wave-length and that at 4050A rose on prolonged irradiation from an initial value of 0.6 to a constant value of about 8. Between 4000 and 2900A the yield was of constant order of magnitude, but appeared to fall off by about 10-20 per cent in going from the visible toward the shorter wave-lengths.[105] The observation that a definite reaction can take place at 5400-5500A is of interest in view of earlier discussions (Chapter 15) regarding the existence of a threshold wave-length for this reaction.[106]

Hertel assumed the primary process to be the formation of excited chlorine molecules under the influence of light in the band region. A small fraction of these molecules is then dissociated by impact with molecules of either hydrogen, chlorine or of hydrogen chloride. The efficiencies of these molecules in effecting dissociation were found to be in the ratio of 1 : 3 : 0.5. As a result of this dissociation, chains are set up as in the continuous region. The quantum yield in the region between 4850 and 5090A was found to be about half that observed by light in the continuous region. Hertel believed it would be very difficult to determine whether the reaction could proceed at wave-lengths longer than 5000A since the absorption is so low in this region. He noted that Dhar and Bhagwat had found a limiting zone at 6650A, and believed that a slight reaction might occur at 7700A.

[97] Bates, J. R., *Proc. Nat. Acad. Sci.*, **19**, 81 (1933).
[98] Geib, K. H., and Harteck, P., *Z. physik. Chem.*, **15B**, 116 (1931).
[99] Kokochashvili, V., *Z. physik. Chem.*, **23B**, 431 (1933).
[100] Rollefson, G. K., *J. Chem. Physics*, **2**, 144 (1934).
[101] Farkas, L., and Farkas, A., *Naturwiss.*, **22**, 218 (1934).
[102] Bodenstein, M., and Schenk, P. W., *Z. physik. Chem.*, **20B**, 420 (1933).
[103] Allmand, A. J., and Beesley, E., *J. Chem. Soc.*, 2693, 2709 (1930).
[104] Bateman, J. B., and Allmand, A. J., *J. Chem. Soc.*, 157 (1934).
[105] See also Norrish, R. G. W., and Ritchie, M., *Proc. Roy. Soc.*, **140**, 99, 112, 713 (1933).
[106] Hertel, E., *Z. physik. Chem.*, **14**, 443; **15**, 325 (1932).

Recently Allmand and Craggs[107] have found it possible to form hydrogen chloride when mixtures of 0.1-0.6 mm. of hydrogen and 1.7 to 166 mm. of chlorine are irradiated with light of 5460A, a slightly longer wave-length than corresponds to the dissociation of chlorine into normal atoms. It would be expected that if excited molecules are formed and dissociated on impact with other molecules the absorbed energy of excitation must supply most of the energy for the subsequent dissociation. The slight deficiency involved when 5460A is used can, however, be supplied otherwise. If the chlorine molecules which absorb this energy are initially in high vibrational levels they can acquire sufficient energy by the absorption of this wave-length. The results could, it was believed, be correlated with the continuous background of the banded absorption spectrum of chlorine. No reaction occurred at 5790A. From the temperature coefficient of the reaction at 5460A, the activation energy appeared to be 9.78 kcal. The quantum efficiency relative to unity at 4360A was approximately 0.3. Subsequent to a more recent interpretation of the continuous absorption spectrum of chlorine, Bayliss has shown that at all wave-lengths the primary process is the same—dissociation—and that the quantum yield, temperature coefficient and activation energy are independent of the wave-length of the exciting radiation.[108]

In addition to the investigations in which temperature coefficients have been determined for calculations of activation energies, there have been a few earlier observations of temperature coefficients to which very brief reference may be made. Padoa and Butironi[109] seem to have been the first to make such determinations. They found the acceleration produced by increase in temperature to be but small in the ultraviolet, greater for violet and blue light and a maximum for green light. The values were: green (5500-5300A), 1.50; blue (4900-4700A), 1.31; violet (4600-4400A), 1.21; ultraviolet (4000-3500A), 1.17. Hertel's observations gave 1.48 in the band region in good agreement with those of Padoa. The values obtained by Livingston and Lind[110] were somewhat lower.

Lavrov[111] has made many determinations of the critical pressures at which the carbon arc will ignite various mixtures of chlorine, hydrogen and various gases.

[107] Allmand, A. J., and Craggs, H. C., *J. Chem. Soc.*, 241 (1936).
[108] Aickin, R. G., and Bayliss, N. S., *Trans. Faraday Soc.*, **33**, 1333 (1937); Bayliss, N. S., *Ibid.*, **33**, 1339 (1937).
[109] Padoa, M., and Butironi, C., *Atti accad. Lincei*, **24** (II), 215 (1916); *Chem. Abs.*, **11**, 1356 (1917).
[110] Livingston, R., and Lind, S. C., *J. Am. Chem. Soc.*, **52**, 593 (1930).
[111] Lavrov, F. A., and Zagulin, A. V., *Acta Physicochim. U.R.S.S.*, **1**, 979 (1934); *Brit. Chem. Abs.*, **A**, 943 (1936); Lavrov, F. A., and Perel'man, T., *Acta Physicochim. U.R.S.S.*, **2**, 91 (1935); *Chem. Abs.*, **29**, 6506 (1935).

Chapter 19

Reactions of Inorganic Gases Other than Halogen Halides

Reactions of Oxygen

The Oxygen-Ozone Transformation. Schönbein, who was the discoverer of ozone, reported that oxygen can be photochemically activated [1] and Nernst [2] interpreted the formation of ozone by the silent electric discharge as a photochemical reaction. Lenard [3] observed formation of ozone in air by the action of sparks from a Leyden jar and demonstrated that it was due to light of wave-lengths less than 2000A. Goldstein [4] succeeded in preparing a dark blue liquid containing a high percentage of ozone within a discharge tube containing oxygen and immersed in liquid air.

With the advent of quartz mercury arcs, reports began to appear regarding the conditions under which a considerable yield of ozone could be produced in air by ultraviolet radiations. Fischer and Braehmer [5] described an apparatus in which electrolytic gas was conducted through an annular narrow space surrounding a quartz-contained mercury arc, the entire apparatus being cooled by immersion in water. Their measurements of the yield of ozone produced under different conditions of operation indicated its formation to be opposed by a reverse reaction, the speed of the latter increasing rapidly with rise of temperature. Warburg and Regener [6] had previously shown the silent discharge and the short wave-length radiations of sparks to possess both ozonizing and deozonizing properties and Regener [7] had shown that the deozonizing effect is produced by wave-lengths absorbed by glass but not by quartz. Regener found that a concentration of 2.2 per cent ozone could be produced by irradiating oxygen with the light from an aluminum spark, the chief intensity of which lies between 1719 and 1884A. The same stationary concentration was also produced when a gas containing a concentration of 6 per cent of ozone (prepared by the action of a silent discharge) was irradiated by the spark. The scant absorption data then available indicated that the ozone was chiefly formed by radiations of 2000A or less and that it was decomposed by wave-lengths between 2000 and 3000A.

Chapman, Chadwick and Ramsbottom [8] obtained considerable yields of ozone by the action of ultraviolet rays on partially dried oxygen, using a manometric method for following the reaction. At about this period several patents were

[1] Schönbein, C., *J. prakt. Chem.*, **75,** 99 (1858).

[2] Nernst, W., *Jahresber. Elektr. Ges.*, 38 (**1894**), cited by Plotnikow, J., "Allgem. Photochemie," de Gruyter, Berlin, **1936,** 565.

[3] Lenard, P., *Ann. Physik,* **1,** 486 (1900).

[4] Goldstein, E., *Ber.,* **36,** 3042 (1903).

[5] Fischer, F., and Braehmer, F., *Ber.,* **38,** 2633 (1905).

[6] Warburg, E., and Regener, E., *Sitzber. K. Akad. Wiss. Berlin,* 1228, **1904**; *J. Chem. Soc.,* **86,** (ii), 692 (1904).

[7] Regener, E., *Ann. Physik,* **20,** 1033 (1906). For a recent theoretical discussion of the equilibrium between ozone formation and decomposition, see Eucken, A., and Patat, F., *Z. physik. Chem.,* **33B,** 459 (1936).

granted for the production of ozone in various types of apparatus by the action of ultraviolet radiations.[9]

The formation of ozone in the vicinity of quartz mercury arcs is now a familiar observation. Dadlez [10] measured the diminution of the ozone content of the air at increasing distances from lamps of various makers to determine whether ozone is formed in sufficient amount to constitute a health hazard to operators of these lamps. He found that concentrations not greater than 0.05-0.3 mg. per cubic meter are produced under favorable conditions. Symptoms of distress are produced only when the concentration reaches 1.0 to 1.5 mg. per cubic meter and 4 mg. per cubic meter are necessary to render the atmosphere unsupportable to life. Nevertheless, Cornelius [11] recommended filtration to eliminate the rays forming ozone, at least in drying patent leather.

The formation of ozone by the shortest wave-lengths of the mercury arc, chiefly the 1850A line, may be now considered in the light of early work on the band spectra of oxygen. A series of bands in the Schumann region observed and measured by Schumann [12] and by Runge [13] are known as the Schumann-Runge bands. They begin at about 1925 to 2026A according to Leifson,[14] and converge to a limit at 1751A.[15] Detailed term analyses of these bands have been given by Ossenbrüggen.[16] Flory [17] believes the O_2 molecule predissociates in the band region above 1751A into normal ^3P atoms. Quantitative absorption data by Ladenburg, Van Voorhis and Boyce [18] and by Granath [19] indicate that the limit is followed by a region of continuous absorption which has its maximum at 1450A, and continues to nearly 1300A.[20] It has been subsequently shown that the products of the dissociation which occurs at or beyond 1751A are a normal ^3P and an excited ^1D oxygen atom.[21] Frerichs [22] found the excitation energy of the ^1D oxygen atom to be 1.96 e-volt. When this energy is deducted from that which corresponds to the convergence limit (7.05 volts), the heat of dissociation of oxygen into two normal atoms is found to be 5.09 e-volts, which corresponds to 117.3 kcal. or 2429A. Data on the kinetics of the reaction produced by the mercury line at 1850A are not available. Working with radiations of wave-lengths 1862 to 1719A, Eucken [23] found a negative temperature coefficient for the conversion of oxygen at very low pressures into ozone at temperatures between those of the room and liquid air.

[8] Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., *J. Chem. Soc.,* **91,** 947 (1907); see also Bordier, H., and Nogier, T., *Compt. rend.,* **147,** 354 (1908) and v. Aubel, E., *Ibid.,* **149,** 983 (1909); **150,** 96 (1910).

[9] Potter, H. N., U. S. P. 854,965, May 28, 1907; Jaubert, G. F., French P. 415,574, July 19, 1909; Davis, N. W., U. S. P. 1,209,132, Dec. 19, 1916; *Chem. Abs,* **11,** 549 (1917).

[10] Dadlez, J., *Compt. rend.,* **185,** 89 (1927); *L'Union Pharm.,* **69,** 17 (1928); *Chem. Abs.,* **23,** 2660 (1929).

[11] Cornelius, F., *Chim. et Ind.,* **6,** 218 (1921); German P. 318,065, Nov. 15, 1916.

[12] Schumann, V., *Smithsonian Contributions to Knowledge,* **29,** No. 1413 (1903).

[13] Runge, C., *Physica,* **1,** 254 (1921).

[14] Leifson, S. W., *Astrophys. J.,* **63,** 73 (1926); Hopfield, J. J., and Leifson, S. W., *Phys. Rev.,* **25,** 716 (1925).

[15] Birge, R. T., and Sponer, H., *Phys. Rev.,* **28,** 259, 270 (1926).

[16] Ossenbrüggen, W., *Z. Physik,* **49,** 167 (1928).

[17] Flory, P. J., *J. Chem. Physics,* **4,** 23 (1936).

[18] Ladenburg, R., Van Voorhis, C. C., and Boyce, J. C., *Phys. Rev.,* **40,** 1018 (1932); Ladenburg has also reviewed the work on absorption by atmospheric oxygen. *J. Opt. Soc. Am.,* **25,** 259 (1935).

[19] Granath, L. P., *Phys. Rev.,* **34,** 1046 (1929).

[20] Stueckelberg, E. C. G., *Phys. Rev.,* **42,** 518 (1932).

[21] Herzberg, G., *Z. physik. Chem.,* **4B,** 223 (1929).

[22] Frerichs, R., *Phys. Rev.,* **36,** 398 (1930).

[23] Eucken, A., *Z. physik. Chem.,* **107,** 436 (1923).

The absorption data thus far considered are not adequate to explain the results of Warburg on the formation of ozone by the irradiation of oxygen in a streaming system with the lines 2070 and 2530A.[24] These wave-lengths are longer than the Schumann-Runge bands and in order to secure sufficient absorption for a reaction to occur, it was necessary to employ the oxygen at high pressures. With the wave-length 2070A, Warburg found a quantum yield of 3.1 when the oxygen pressure was 125 kg. per square cm., and somewhat lower values at pressures as high as 300 kg. With the longer wave-length, 2530A, the quantum yields were somewhat lower and the same drop was observed with increase in pressure. Warburg attributed the decrease in yield with increase in pressure to some influence of adjacent molecules upon each other which affected their ability to absorb radiations. The absorption of the 2070A line was found to increase nearly seven times when the pressure was raised from about 30 to 325 kg. per square cm.[25] Noyes,[26] who has given a critical historical discussion of the reaction, believes, however, that the observed pressure effect on the quantum yield was not much greater than the possible experimental errors.

To account for the quantum yield of three, Warburg suggested, in the case of the 2070A line, a primary dissociation into atoms. This, however, is in disagreement with the subsequent findings upon the convergence limit of the Schumann-Runge bands. Warburg recognized that the 2530A line could not produce a dissociation of oxygen and suggested that a mechanism involving excited molecules would be necessary.

Further interpretations of the results of Warburg have been given by Wulf,[27] who has pointed out that the oxygen molecule does not absorb in the regions Warburg found effective. Certain weak bands which have been found in long paths of oxygen at ordinary pressures[28] and in compressed or liquid oxygen[29] appear to converge to a limit at 2429A. This agrees with the energy required for the dissociation of oxygen into normal atoms. The weak bands are followed by a weak continuous region which extends to shorter wave-lengths and even underlies the Schumann-Runge bands. Wulf believes that the light of wave-length 2070A, in Warburg's experiments was absorbed by this continuum. He ascribes the new bands, at least in part, to a van der Waals molecule, O_4, the presence of which in highly compressed oxygen had previously been suggested by Lewis[30] from a consideration of the magnetic susceptibility of oxygen at low temperatures. In support of this, Wulf cites the fact that the absorption intensity at 2470A increases as the square of the oxygen pressure. From an extrapolation of data of Liveing and Dewar,[31] he computed the region of the beginning of the continuous spectrum following the bands to be near 2470A, which he thought might correspond to dissociation into an ozone molecule and an oxygen atom. Guillien[32] also interprets data on the absorption of liquid oxygen as indicative of an equilibrium between O_2 and O_4 molecules. A set of bands lying in the region of the convergence of the Herzberg bands has been found by Finkelnburg and Steiner[33] to vary in intensity with the square of the pressure, although they attributed the effect to the proximity of two oxygen molecules rather than to the formation of O_4.[34] The arguments for and against polymerization have been critically discussed by Wulf.[35] A final conclusion between the possibility of the existence of O_4 and absorption by a pair of O_2 molecules during collision has not been reached. Steiner[36] does not believe the oxygen molecule should be considered a free radical, despite its paramagnetism, since the spin interaction between two oxygen molecules has a very low energy, not of the order of magnitude involved in chemical reaction.

[24] Warburg, E., *Sitzb. Akad. Wiss.*, 216 (**1912**); 872 (**1914**); *Z. Elektrochem.*, **27**, 133 (1921).

[25] Warburg, E., *Sitzb. Akad. Wiss. Berlin*, 230, **1915**; *J. Chem. Soc.*, **118** (ii), 404 (1920).

[26] Noyes, W. A., Jr., *Rev. Modern Physics*, **5**, 283 (1933).

[27] Wulf, O. R., *Proc. Nat. Acad. Sci.*, **4**, 356 (1928); **14**, 609 (1928); *J. Opt. Soc. Am.*, **25**, 231 (1935).

[28] Herzberg, G., *Naturwiss.*, **20**, 577 (1932).

[29] Ciechomski, L., *Beibl. Ann. Physik*, **39**, 240 (1915); Shaver, W. W., *Proc. Roy. Soc. Canada*, **15**, (III), 7 (1921). For the absorption of solid oxygen, see Prikhot'ko, A., Ruhemann, M., and Federitkenko, A., *Physik. Z. Sowjetunion*, **7**, 410 (1935); *Chem. Abs.*, **29**, 6141 (1935).

[30] Lewis, G. N., *J. Am. Chem. Soc.*, **46**, 2027 (1924).

[31] Liveing, G. D., and Dewar, Sir J., *Proc. Roy. Soc.*, **46**, 222 (1889).

[32] Guillien, R., *Compt. rend.*, **198**. 1486 (1934).

It has been claimed by Dickinson and Sherill[37] that the formation of ozone at atmospheric pressure can be stimulated by the presence of excited mercury atoms. Collision of an oxygen molecule with an excited mercury atom can give it nearly the energy necessary for dissociation into normal atoms[37a] or the excited mercury atom may on collision produce an excited oxygen molecule.

Radiations passing through fluorite (average wave-length 1750A and therefore close to or shorter than the convergence limit of the Schumann-Runge bands) form ozone in oxygen at atmospheric pressure with a quantum efficiency of two.[38] In the region of the bands the primary process has been believed to be the formation of an excited molecule followed by reactions as indicated in the scheme:

$$O_2 + h\nu \longrightarrow O_2^*$$
$$O_2^* + O_2 \longrightarrow O_3 + O$$
$$O + O_2 \longrightarrow O_3$$

The latter two processes are assumed to occur on the walls or as a result of triple collisions. In the region of continuous absorption, two oxygen atoms, one excited (^1D) are produced, and each then is assumed to combine with an oxygen molecule. If, as Flory suggests, the primary process is one of predissociation, the first equation would yield oxygen atoms directly, eliminating the necessity for the second equation.

The Decomposition of Ozone. Ozone possesses absorption bands both in the visible and in the ultraviolet regions and decomposition can be effected by absorption of light in either of these regions. Although the first investigations were conducted in the ultraviolet range, it is simplest to begin with the effects of visible light.

Ladenburg and Lehmann[39] showed ozone to possess a group of visible absorption bands,[40] for which Colange[41] has given quantitative absorption data. The diffuseness of the bands indicates the occurrence of predissociation.

[33] Finkelnburg, W., and Steiner, W., *Z. Physik*, **79**, 69 (1932).

[34] See also Steiner, W., *Trans. Faraday Soc.*, **30**, 34 (1934) and Salow, H., and Steiner, W., *Z. Physik*, **99**, 137 (1936).

[35] Wulf, O. R., *J. Am. Chem. Soc.*, **50**, 2596 (1928).

[36] Salow, H., and Steiner, W., *Nature*, **134**, 463 (1934).

[37] Dickinson, R. G., and Sherill, M. S., *Proc. Nat. Acad. Sci.*, **12**, 175 (1926); for a detailed discussion see Franck, J., *J. Phys. Chem. U.S.S.R.*, **5**, 1013 (1934).

[37a] Presumably the deficit is made up thermally.

[38] Vaughan, W. E., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **52**, 559 (1930); Groth, W. [*Z. physik. Chem.*, **37B**, 307 (1937)] finds it 1.90 for the xenon lines 1295 and 1470A.

[39] Ladenburg, R., and Lehmann, E., *Ann. Physik*, **21**, 305 (1906).

[40] See also Wulf, O. R., *Proc. Nat. Acad. Sci.*, **16**, 508 (1930).

[41] Colange, G., *J. Phys. Radium*, **8**, 254 (1927).

[42] Griffith R. O., and Shutt, W. J., *J. Chem. Soc.*, **119**, 1948 (1921); **123**, 2752 (1923).

By the use of filters, Griffith and Shutt [42] concluded the most effective spectral regions to lie between 7600 and 6700A and between 6150 and 5100A. The decomposition rate was proportional to the square of the ozone concentration. They believed the reaction to be catalyzed by hydrogen. Some water formation was also observed in accordance with the reaction $H_2 + O_3 \rightarrow H_2O + O_2$. This latter reaction became predominant when the original ozone concentration was below 2.4 per cent. In the presence of carbon monoxide,[43] some carbon dioxide was produced in an analogous reaction, which, however, occurred to but a slight extent. The simple ozone decomposition was said to be catalyzed by foreign gases in the following decreasing order of effectiveness: hydrogen, (far more effective than the others), helium, argon, nitrogen, carbon monoxide, and carbon dioxide. These authors believed the mechanism of the decomposition to involve the formation of activated molecules of ozone. These were then thought to combine each with an ozone molecule in its ground state to form a complex which, on collision with other molecules, might dissociate to yield from each complex three oxygen molecules. The temperature coefficient of the reaction was found to increase with the wave-length.

Similar results were reported by Kistiakowsky,[44] who employed monochromatic light of 6200A, used mixtures containing up to 70 per cent of ozone and varied the total gas pressures from atmospheric down to 9 mm. He found the quantum yields to be greater than two, and a direct function of the amount of red light absorbed and of the effective pressure of ozone in the system. He believed that in the absence of other added gases oxygen acted as an effective deactivator of excited ozone molecules and that those gases which, like hydrogen, seemed to catalyze the decomposition, appeared to do so only because they were less effective inhibitors than oxygen.

Schumacher [45] proposed a mechanism involving a photodissociation of the ozone into an oxygen molecule and an oxygen atom. Visible light is energetically capable of effecting this process, which requires 24.6 kcal., although this was not known at the time of Kistiakowsky's first paper. The foreign gas inhibitions were attributed to their specific effects on the recombination of the dissociation products to form ozone in three-body collisions. In the case of hydrogen, an interaction of the oxygen atom with the hydrogen molecules to form water was suggested as the cause of the ten-fold increase in the velocity of the ozone decomposition.

The strong absorption of ozone in the ultraviolet region has been the subject of numerous investigations, some of which have been discussed in Chapter 10. The maximum lies at about 2550A. According to Wulf and Melvin,[46] the spectrum appears partly banded and partly continuous; the bands, of which there are 23 of weak intensity between 3050 and 3400A, become sharper at low temperatures. Schumacher [47] believes an underlying continuum may be due to dissociation into an oxygen molecule in the ground state and an excited oxygen atom, or *vice versa*. Kondratjew [48] suggests that at wave-lengths less than 2700A both dissociation

[43] Griffith, R. O., and McWillie, J., *J. Chem. Soc.*, **123**, 2767 (1923); Griffith, R. O., and McKeown, A., *Trans. Faraday Soc.*, **21**, 597 (1926).

[44] Kistiakowsky, G. B., *Z. physik. Chem.*, **117**, 337 (1925).

[45] Schumacher, H. J., *J. Am. Chem. Soc.*, **52**, 2377 (1930); Schumacher, H. J., and Sprenger, G., *Z. physik. Chem.*, **11B**, 38 (1930); *Z. Elektrochem.*, **38**, 620 (1932).

[46] Wulf, O. R., and Melvin, E. H., *Phys. Rev.*, **38**, 333 (1930).

[47] Schumacher, H. J., *J. Am. Chem. Soc.*, **52**, 2389 (1930).

[48] Kondratjew, V., *Z. physik. Chem.*, **7B**, 70 (1930); Jakolewa, A., and Kondratjew, V., *Physik. Z. Sowjetunion*, **1**, 472 (1932).

products may be in excited states. Mecke,[49] admits this possibility but places the wave-length limit at 2655A.[50]

Early observations upon the rate of the decomposition of ozone in ultraviolet light were reported by v. Bahr [51] and by Weigert.[52] In the presence of hydrogen, a catalysis was observed.

Using the wave-length 2530A, Warburg [53] measured the quantum yield of the reaction under various conditions. For low concentrations of ozone, about 0.5 per cent or less, the yield was 0.28. It was considerably greater in the presence of nitrogen (1.1) or helium (1.7). For high ozone concentrations, the yields increased to 3.5 at 9 per cent. With moist ozone at about this concentration, the use of the wave-length 2090A gave a quantum yield as high as 8, suggesting a chain reaction.

Schumacher and Beretta [54] find the mechanism of the reaction due to the wave length 3130A to be similar to that occurring in red light. Heidt and Forbes [55] find from the magnitude of the quantum efficiency of the decomposition of pure, dry ozone that even in the absence of water vapor the reaction produced by 2080, 2540 or 2800A has chain characteristics. The yields were frequently above two, sometimes four and even as high as 6.7. The quantum efficiency increased with the partial pressure of ozone and decreased with that of oxygen. No dependence of the quantum yield upon the wave-length was observed. The temperature coefficient was 1.2, or possibly slightly greater at very low temperatures. Heidt [56] later found approximately the same quantum yields at 3130A as at 2080A.

The Chlorine-Sensitized Decomposition of Ozone. In regions in which ozone does not absorb, its decomposition can be brought about by the addition of chlorine as a photosensitizer. This reaction was discovered by Weigert,[57] who concluded its rate to be proportional to the light absorbed by the chlorine and independent of the ozone concentration. Bonhoeffer [58] found the absorption of one quantum (4360 or 4050A) to produce the decomposition of two molecules of ozone. More recent observations by Allmand and Spinks [59] have shown quantum yields as high as 30 (in some cases 59) at high ozone concentrations. Under these conditions the rate of reaction is proportional to the square root of the light intensity. Schumacher and Wagner [60] suggested the formation of ClO as an intermediate product in this reaction, and Bodenstein, Harteck and Padelt [61] gave evidence for the formation of some ClO_3. There are many complicating features, as an induction period (not observed by Weigert) and after effects. Allmand and Spinks suggested that

[49] Mecke, R., *Z. physik. Chem. Bodenstein Festband*, 392 (1931).

[50] For further details on the absorption spectrum of ozone in the ultraviolet, see Lauchli, A., *Helv. phys. Acta*, **1**, 232 (1928); *Z. Physik*, **53**, 92 (1929); Dutheil, J. and M., *J. Phys. Radium*, **7**, 415 (1926); Cabannes, J., and Dufay, J., *J. Phys. Radium*, **7**, 257 (1926); Chalonge, D., and Lambrey, M., *Compt. rend.*, **184**, 1165 (1927); Tsi-Zé, N., and Shin-Piaw, C., *Compt. rend.*, **195**, 309 (1932); Vassy, E., *Compt. rend.*, **202**, 1426 (1936).

[51] v. Bahr, E., *Ann. Physik*, **33**, 598 (1910).

[52] Weigert, F., *Z. physik. Chem.*, **80**, 78 (1912); *Ber.*, **46**, 815 (1913); Weigert, F., and Böhm, H., *Z. physik. Chem.*, **90**, 189 (1915).

[53] Warburg, E., *Sitzb. Preuss. Akad.*, 644 (1913).

[54] Schumacher, H. J., and Beretta, U., *Z. physik. Chem.*, **17B**, 405, 417 (1932); Ritchie, M., *Proc. Roy. Soc.*, **146A**, 848 (1934).

[55] Heidt, L. J., and Forbes, G. S., *J. Am. Chem. Soc.*, **56**, 2365 (1934).

[56] Heidt, L. J., *J. Am. Chem. Soc.*, **57**, 1710 (1935).

[57] Weigert, F., *Ann. Physik*, **24**, 243 (1907); *Z. Elektrochem.*, **14**, 591 (1908).

[58] Bonhoeffer, K. F., *Z. Physik*, **13**, 94 (1923).

[59] Allmand, A. J., and Spinks, J. W. T., *Nature*, **124**, 651 (1929); *J. Chem. Soc.*, 1652 **(1931)**; 599 **(1932)**.

[60] Schumacher, H. J., and Wagner, C., *Z. physik. Chem.*, **5B**, 199 (1929).

[61] Bodenstein, M., Harteck, P., and Padelt, E., *Z. anorg. Chem.*, **147**, 233 (1925).

chlorine atoms, formed in the primary absorption process, may combine to ClO_3 on collision with ozone molecules and that a chain reaction may ensue and be terminated by the absorption of intermediate atoms or groups on the walls. Furthermore, some ClO_3 molecules may unite to form chlorine hexoxide which in the presence of water forms chloric and perchloric acids. The combination of Cl atoms and oxygen molecules may also give rise to ClO_2. The latter, reacting with ozone, forms oxygen molecules and ClO_3 groups.

Heidt, Kistiakowsky and Forbes [62] found highly abnormal temperature coefficients ranging from 0.7 to 14.6. The purer the gases the more erratic were the results and the more prominent a "fast" reaction in the dark following a brief exposure to light. A marked decrease in the rate with the time of illumination was also observed. No mechanism could be proposed capable of explaining the results. In a subsequent investigation, Norrish and Neville [63] observed a red liquid oxide of chlorine $(ClO_3)_n$ and suggested that its separation and slow decomposition might in some manner account for the observations of Heidt, Kistiakowsky and Forbes. Norrish and Neville found that at low ozone concentrations, the reaction is of zero order and has a chain mechanism. At high ozone concentrations, in agreement with Allmand and Spinks, the rate was proportional to the square root of the light intensity (3650A). At high concentrations of oxygen and chlorine, the rate was proportional to the first power of the intensity and the reaction was inhibited. The quantum yields varied from two to about ten. Chains may be propagated both by chlorine atoms and by ClO radicals. Nitrogen and carbon dioxide appeared to have no effect on the reaction. Rollefson and Byrns [64] isolated ClO_3 from the reaction mixture and noted that its occurrence therein prevents pressure measurements from affording an accurate indication of the amount of ozone decomposed. They also produced evidence for a reaction mechanism involving Cl_2O_7.

The chlorine-sensitized decomposition of ozone was used in actinometry by Cremer [65] since when low ozone concentrations are employed and light absorbed only by chlorine is used, the quantum yield is generally found to be two. Even in carbon tetrachloride solution, quantum yields of two have been observed for both the unsensitized and the sensitized ozone decompositions.[66]

The effect of irradiation of ozone-chlorine mixtures by wave-lengths absorbed by the ozone rather than by the chlorine has been investigated by Bodenstein and Schumacher,[67] who proposed a mechanism involving directly excited ozone molecules. These were thought to react with chlorine molecules with the formation of the ClO radical and ClO_2. They found also that chlorine hexoxide was produced and that its yield could be increased by lowering the temperature or by increasing the size of the reaction vessel.

The Formation and Decomposition of Water

Absorption. Water vapor commences to absorb light quite suddenly at about 1800A.[68] Rathenau [69] found predissociation bands between 1780 and 1540A and

[62] Heidt, L. J., Kistiakowsky, G. B., and Forbes, G. S., *J. Am. Chem. Soc.*, **55**, 223 (1933).
[63] Norrish, R. G. W., and Neville, G. H. J., *Nature*, **131**, 544 (1933); *J. Chem. Soc.*, 1864 (1934).
[64] Rollefson, G. K., and Byrns, A. C., *J. Am. Chem. Soc.*, **56**, 364 (1934).
[65] Cremer, E., *Z. physik. Chem.*, **128**, 285 (1927).
[66] Bowen, E. J., Moelwyn-Hughes, E. A., and Hinshelwood, C. N., *Proc. Roy. Soc.*, **134A**, 211 (1931).
[67] Bodenstein, M., and Schumacher, H. J., *Z. physik. Chem.*, **5B**, 233 (1929).
[68] [1830A in 17 mm. layers of liquid water, Kreusler, H., *Ann. Physik*, **6**, 412 (1901)]; Leifson, S. W., *Astrophys. J.*, **63**, 73 (1926); Goodeve, C. F., and Stein, N. O., *Trans. Faraday Soc.*, **27**, 193 (1931).
[69] Rathenau, G., *Z. Physik*, **87**, 32 (1933).

again at 1340A. Mecke [70] believes there is a series of bands converging at 1390A, corresponding to a dissociation into an excited hydroxyl radical and a hydrogen atom. A continuous region near 1800A may correspond to a dissociation into a hydrogen atom and a normal state hydroxyl radical. Quantitative data on the absorption of water in the longer wave-length ultraviolet and in the visible have been given by Granath [71] and by Dawson and Hulburt.[72]

According to Plotnikow, the first observation of the photo-chemical decomposition of water into hydrogen and oxygen was made by Baker.[73] Similar observations were made by early workers with the quartz mercury arc.[74] Tian,[75] who obtained traces of hydrogen peroxide, clearly recognized that only the shortest waves passing through quartz were capable of effecting the decomposition of water. Dhar [76] believes water vapor in the upper atmosphere to be decomposed by the solar ultraviolet.

Coehn [77] described the production of a stationary state in which irradiation of water vapor caused a decomposition of 0.2 per cent; the decomposition increased with the light intensity and decreasing pressure. Andrejeff,[78] however, found that at 200°C., in the stationary state, decomposition had proceeded to only 0.002 per cent. No theoretical studies from the modern viewpoint are available.

The formation of hydrogen peroxide from water and oxygen by ultraviolet rays has been observed. It appeared to depend largely upon special experimental conditions or possibly upon the presence of impurities.[79]

Earlier workers claimed to have been able to induce the combination of hydrogen and oxygen by exposure to the ultraviolet radiations of a mercury arc. Although Thiele [80] believed the presence of moisture not to be necessary for the combination to occur, Baker and Carlton [81] were unable to observe any contraction during irradiation for five or six hours of gases which had been dried several weeks. Wet gases showed a certain amount of reaction during the same period of irradiation.

Kistiakowsky [82] investigated the reaction in two wave-length regions, the source being a condensed spark between aluminum disk electrodes. When the lines about 1720A, that is, within the continuous absorption region of oxygen, were employed, the yield of ozone in the presence of hydrogen was only one-fourth of that in the presence of nitrogen and an equal amount of hydrogen peroxide was also formed. The ozone yields were proportional to the relative concentrations of oxygen in the hydrogen-oxygen mixture, and the yields of hydrogen peroxide were proportional to the concentration of hydrogen. In the more recent experiments it was found that in the presence of increasing concentrations of hydrogen, the ozone yield decreased to zero and the yield of hydrogen peroxide increased. At

[70] Mecke, R., *Trans. Faraday Soc.*, **27**, 369 (1931).
[71] Granath, L. P., *Phys. Rev.*, **34**, 1046 (1929).
[72] Dawson, L. H., and Hulburt, E. O., *J. Opt. Soc. Am.*, **24**, 175 (1934).
[73] Baker, H. B., *Proc. Chem. Soc.*, **18**, 40 (1902).
[74] Fischer, F., and Braehmer, F., *Ber.*, **79**, 958 (1906); Thiele, H., *Ber.*, **40**, 4914 (1907); *Z. angew. Chem.*, **22**, 2472 (1909); Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1191 (1910); **152**, 522 (1911); Smits, A., and Aten, A., *Z. Elektrochem.*, **16**, 264 (1910).
[75] Tian, A., *Compt. rend.*, **152**, 1483 (1911); **151**, 1040 (1911).
[76] Dhar, N. R., *Trans. Faraday Soc.*, **30**, 142 (1934).
[77] Coehn, A., *Ber.*, **43**, 880 (1910).
[78] Andrejeff, I., *Z. Elektrochem.*, **19**, 551 (1913).
[79] Kernbaum, M., *Compt. rend.*, **148**, 705 (1909); **149**, 116, 273 (1909).
[80] Thiele, H., *Z. angew. Chem.*, **22**, 2472 (1909).
[81] Baker, H. B., and Carlton, M., *J. Soc. Chem. Ind.*, **44**, 1047 (1925).
[82] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **52**, 1868 (1930); Kistiakowsky, G. B., and Smith, H. A., *Ibid.*, **57**, 835 (1935).

high pressures, the yield of water parallels that of hydrogen peroxide. At lower pressures, the yield of water also increases, although not at the expense of ozone or peroxide. In a one to one oxygen-hydrogen mixture, the rates at which the excited oxygen atoms react with oxygen or hydrogen are nearly equal. The following system of partial reactions was suggested:

$$O + O_2 \longrightarrow O_3 \quad (1)$$
$$O + H_2 \longrightarrow OH + H \quad (2)$$
$$H + O_2 \longrightarrow HO_2 \quad (3)$$
$$OH + OH \longrightarrow H_2O_2 \quad (4)$$
$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \quad (5)$$
$$OH + HO_2 \longrightarrow H_2O + O_2 \quad (6)$$

It was believed that (2) did not occur readily, the hydrogen molecule showing an unexpected stability. However, the possibility that oxygen atoms might unite with hydrogen in three-body collisions with oxygen molecules appeared to be admissible, (2) and (3) occurring together as

$$O + O_2 + H_2 \longrightarrow OH + HO_2.$$

Kistiakowsky and Smith believed, contrary to Ritchie,[83] that reaction (1) has an activation energy of zero. Nevertheless, the formation of ozone was also thought to take place in triple collisions

$$O + O_2 + O_2 \longrightarrow O_3 + O_2.$$

In later experiments (1935) it was possible to demonstrate the formation of hydrogen peroxide which had been missed in the earlier experiments (1930), even when wave-lengths of the band region (1854-1862A) were alone employed, the strong aluminum lines at 1720A being removed by an oxygen filter. The yield, however, was only half that produced in the experiments with shorter wave-lengths. It appeared that one-half of the absorbed light of the longer wave-lengths forms ozone irrespective of the composition of the gases, the other half giving rise to the same sequence of reactions as occur under shorter wave-length illumination. To explain this, the primary process was assumed to be the formation of excited oxygen molecules which react with oxygen molecules [84] to give ozone and atomic oxygen, but which suffer only elastic collisions with hydrogen. No attempt was made to determine the rate of water formation in this region.

Flory [85] suggests that in the band region predissociation of oxygen produces two normal state oxygen atoms, and that the differences in the reaction as conducted in the band and continuous regions are to be attributed to the different states of the oxygen atoms formed by predissociation and by dissociation.

Neuĭmin and Popov [86] also studied the reaction in the Schumann region, using hydrogen at 0.1 mm. pressure, and found quantum yields (for peroxide formation) of approximately 0.1. Their mechanism was similar to that subsequently given by Kistiakowsky, except that they believed that in the reaction between excited oxygen atoms and hydrogen molecules, the hydroxyl radical formed (along with a

[83] Ritchie, M., *Proc. Roy. Soc.*, **146A**, 848 (1934).

[84] See also Klemenc, A., and Patat, F., *Naturwiss.*, **18**, 281 (1930).

[85] Flory, P. J., *J. Chem. Physics*, **4**, 23 (1936).

[86] Neuĭmin, H., and Popov, B., *Z. physik. Chem.*, **27B**, 15 (1934). For more recent studies with the xenon lamp, see W. Groth and P. Harteck, *Z. Elektrochem.*, **44**, 621 (1938).

hydrogen atom) was excited with vibrational energy up to 2 electron-volts. They also assumed that the combination of two hydroxyl radicals was a wall reaction. Miyanishi [87] studied the influence of temperature upon the reaction. Kistiakowsky found the formation of water to be greatly increased at high temperatures.

The Mercury-Sensitized Reaction. (See also page 257, chapter 16.) Marshall [88] investigated the mercury-sensitized reaction of hydrogen and oxygen. At 50°C., the fall in pressure of dried gas mixtures ranging in composition from 406 mm. hydrogen and 148 mm. oxygen to 572 mm. hydrogen and 156 mm. oxygen, was 24.7 mm. per minute. The pressure-time curves showed an initial break at a point corresponding with saturation of the gas with water-vapor, after which the curves were linear. When oxygen was present in excess, the rate decreased rapidly as the reaction proceeded. However, in the reaction of stoichiometric mixtures, the rate remained constant. Marshall believed the true temperature coefficient to be near unity, but experimentally many corrections were necessary because the concentration of mercury vapor varied with the temperature and because the quantum yield varied with temperature. For the formation of hydrogen peroxide, the quantum yield was found to be 2.5.[88a] At least 75 per cent of the total yield of products was peroxide. The mechanism suggested involved the reactions,

$$Hg^* + H_2 \longrightarrow Hg + 2H \quad (1)$$
$$H + O_2 \longrightarrow HO_2 \quad (2)$$
$$HO_2 + H_2 \longrightarrow H_2O_2 + H \quad (3)$$
$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (4)$$

Marshall [89] later found the optimum mercury vapor pressure for the formation of hydrogen peroxide to be 0.005 mm. The greater rate of reaction in the presence of higher concentrations of mercury was offset by decomposition of the hydrogen peroxide formed. The rate of the reaction probably varied as the first power of the light intensity. The maximum rate of formation of hydrogen peroxide was 2 gm. per hour.

Frankenburger and Klinkhardt,[90] obtained somewhat different quantum yields at room temperature. The quantum yield for water was greater (1.5-2.5) and that for hydrogen peroxide lower (1-2). They objected to the mechanism proposed by Marshall for the formation of hydrogen peroxide (Reactions 2 and 3) on the ground that the reaction $HO_2 + H_2 \longrightarrow H_2O_2 + H$ is endothermic by 31 kcal. Barak and Taylor reported that this conclusion was based upon an unwarranted assumption, and stated that reactions 2 and 3 are together exothermic. Farkas and Sachsse [91] have shown that hydrogen atoms react with O_2 molecules to produce HO_2 by three-body collisions. It is necessary to build up a mechanism of the type devised by Marshall if the quantum yield of hydrogen peroxide is really two or greater, since a chain mechanism is demanded. If, however, as Frankenburger found, the yield is lower, a chain mechanism is not necessary. Then, however, it would be necessary to account for the higher yields of water, assumed to be formed

[87] Miyanishi, M., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **26**, 70 (1935); *Chem. Abs.*, **29**, 2852 (1935).

[88] Marshall, A. L., *J. Phys. Chem.*, **30**, 34, 1078 (1926); Taylor, H. S., and Marshall, A. L., *Ibid.*, **29**, 842, 1140 (1925).

[88a] This represented a correction of an earlier value of 6.6, in error because of the use of an incorrect value for the transmission of the filter.

[89] Marshall, A. L., *J. Am. Chem. Soc.*, **49**, 2763 (1927).

[90] Frankenburger, W., and Klinkhardt, H., *Trans. Faraday Soc.*, **27**, 431 (1931); *Z. physik. Chem.*, **15B**, 421 (1932); see also Barak, M., and Taylor, H. S., *Trans. Faraday Soc.*, **28**, 569 (1932).

[91] Farkas, L., and Sachsse, H., *Z. physik. Chem.*, **27B**, 111 (1934).

directly and not through hydrogen peroxide, by a chain mechanism, as one proposed by Bonhoeffer and Haber.[92] Frankenburger and Klinkhardt assumed the hydrogen peroxide to be formed by the union of two OH radicals in a three-body collision. Bates,[93] suggested that the discrepancy between the results of Frankenburger and Klinkhardt and those of Marshall may be due to the fact that the former workers used a light intensity a hundred-fold greater than that employed by Marshall. Bates favored the Marshall mechanism.

The amount of mercuric oxide formed in the course of the reaction may exert a considerable effect upon the rate and may influence the results. Noyes[94] found no appreciable reaction between mercury and normal state oxygen atoms. But under conditions in which ozone may be formed, there is a reaction. Noyes also suggested the possibility of the formation of a relatively unstable complex (between excited mercury atoms and oxygen)which may be converted into ozone on collision with oxygen molecules. Franck[95] finds that at pressures of oxygen below 1 cm., the formation of mercuric oxide initiated by excited mercury atoms is proportional to the incident intensity of the resonance line of mercury and to the number of damped collisions of mercury with oxygen. Also, the formation of the oxide was said to be independent of the presence of shorter wave-lengths in the incident radiation. At greater oxygen pressures, mercury oxide is formed when oxygen molecules alone are excited by the lines 1860, 1935 and 1990A, which produce ozone. Therefore, excited mercury is not necessary for the synthesis of mercuric oxide in the presence of ozone.[96]

The velocity of the photosensitized reaction between hydrogen and oxygen is slightly higher than that between deuterium and oxygen, but the temperature coefficients of the two reactions seem to be identical.[97]

The formation of water may also be sensitized by substances other than mercury. The formation of water during the combination of hydrogen and chlorine may be regarded as a reaction in which chlorine is the photosensitizer. In this reaction, Cremer[98] found the rate of formation of water to be proportional to the chlorine concentration. He suggested that an excited chlorine atom could pass its excitation energy over to an oxygen molecule, as could an excited Cl_3 molecule. The excited oxygen molecules might then react to form water by the process: $O_2^* + 2H_2 \longrightarrow 2H_2O$. Norrish[99] doubted this mechanism, since he believed the low excitation energy of the metastable chlorine atom would be insufficient to activate the oxygen molecule sufficiently to enable the latter to react with hydrogen. He stated that the inhibiting effect of oxygen on the hydrogen-chlorine combination is due to the reaction of molecules of oxygen with hydrogen atoms of the chain to form OH radicals. The latter can combine at ordinary temperatures to hydrogen peroxide. He found the peroxide to be produced in appreciable quantities when mixtures of oxygen, hydrogen and chlorine at atmospheric pressure were irradiated with light from a mercury arc. Also, it

[92] Bonhoeffer, K. F., and Haber, F., *Z. physik. Chem.*, **137A**, 263 (1928).

[93] Bates, J. R., *J. Am. Chem. Soc.*, **55**, 426 (1933); *J. Chem. Physics*, **1**, 457 (1933).

[94] Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **49**, 3104 (1927); *Z. physik. Chem.*, **2B**, 445 (1929).

[95] Franck, J., *Compt. rend. Acad. Sci. U.R.S.S.*, **4**, 146 (1933); *Brit. Chem. Abs.*, **A**, 263 (1934); *Acta Physicochim. U.R.S.S.*, **1**, 833 (1934); *J. Phys. Chem. (U.S.S.R.)*, **5**, 1013 (1934); *Chem. Abs.*, **29**, 6507 (1935).

[96] It is also possible for the excited mercury atoms to produce some dissociation of water molecules, when and if present, into hydrogen atoms and normal state hydroxyl radicals. Senftleben, H., and Rehren, I., *Z. Physik*, **37**, 529 (1926); Gaviola, E., *Temas de quim.*, **2**, 173 (1929); *Chem. Abs.*, **24**, 2376 (1930).

[97] Evans, M. G., *J. Chem. Physics*, **2**, 726 (1934).

[98] Cremer, E., *Z. physik. Chem.*, **128**, 285 (1927).

[99] Norrish, R. G. W., *Trans. Faraday Soc.*, **27**, 461 (1931).

was stated[100] that if the partial pressure of chlorine in the mixture is above a certain critical value (temperatures between 0° and 300°C.) exposure of the mixture in glass to the light from a mercury vapor lamp will result in a practically instantaneous explosion with quantitative conversion of the hydrogen and oxygen to water. Below this partial pressure of chlorine, a rapid reaction between the hydrogen and chlorine occurs, only a trace of water being formed. The limiting pressure of chlorine increases rapidly as the lower temperatures are approached. His mechanism involved the reactions:

$$H + H_2 + O_2 \longrightarrow OH + H_2O$$
$$OH + H_2 \longrightarrow H + H_2O.$$

It was reported that the second of these reactions cannot occur spontaneously at temperatures below 400°C. In answering certain objections of Semenoff,[101] Norrish stated that for an explosion to occur, a small volume element of the mixture must become heated to 600°C.

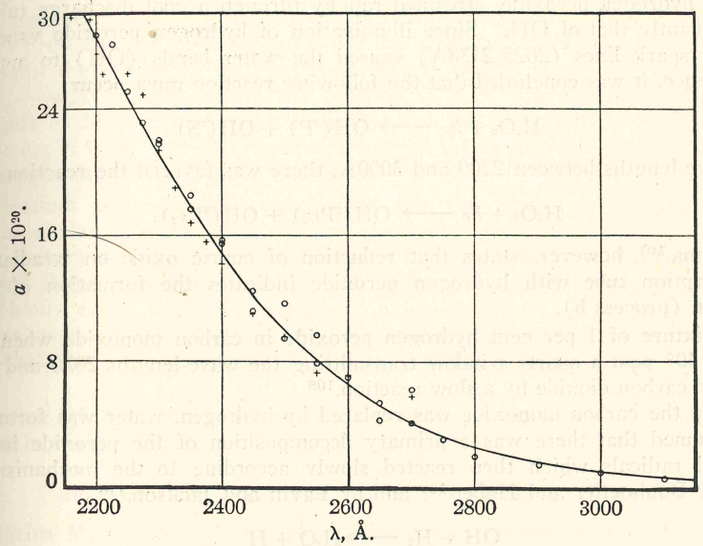


FIGURE 112. Absorption by Hydrogen Peroxide (Urey, Dawsey, and Rice, *Journal American Chemical Society*). +=vapor; o=solution.

Certain nitrogen compounds may also sensitize the reaction of hydrogen and oxygen. Farkas, Haber and Harteck[102] found small quantities of ammonia to increase the reaction velocity at temperatures between 120°C. and 420°C. with and without irradiation by a zinc spark.[103] Taylor and Salley[104] measured the tem-

[100] Norrish, R. G. W., *Nature*, **127**, 853 (1931); *Proc. Roy. Soc.*, **135A**, 334 (1932); *Physik. Z. Sowj.*, **3**, 225 (1933).

[101] Semenoff, N., *Physik. Z. Sowj.*, **3**, 225 (1933).

[102] Farkas, L., Haber, F., and Harteck, P., *Naturwiss.*, **18**, 266 (1930).

[103] See also Taylor, H. S., and Bates, J. R., *Nature*, **125**, 599 (1930) for the formation of atomic hydrogen by the photodissociation of ammonia.

[104] Taylor, H. S., and Salley, D. J., *J. Am. Chem. Soc.*, **55**, 96 (1933).

perature coefficients of the mercury-sensitized and of the ammonia-sensitized reactions at high temperatures. The results indicated that in the presence of ammonia long reaction chains occur above 300°C, but that in the mercury-sensitized reaction lengthening of the chains occurs only above 490°C. The chains may be propagated by atomic hydrogen, amino-radicals, or intermediate oxidation products.

Nitrogen peroxide functions also in photochemical combination of hydrogen and oxygen. On absorption of light the peroxide dissociates into NO and O which then start the reaction chain between hydrogen and oxygen.[105]

The Decomposition of Hydrogen Peroxide. Urey, Dawsey and Rice[106] determined the coefficients of absorption of hydrogen peroxide vapor at room temperature (Figure 112). The continuous nature of the curve indicates a dissociation of the molecules. The peroxide molecule was regarded as formed of two OH radicals. From thermochemical data it did not appear possible to choose between the following methods of dissociation: (a) into 2OH, (b) into H and HO_2 and (c) into H_2O and O. The first possibility was favored since the emission spectrum of hydrogen peroxide, streamed rapidly through a cool discharge tube, was predominantly that of OH. Since illumination of hydrogen peroxide vapor with the zinc spark lines (2025-2138A) caused the water bands (OH) to appear in fluorescence, it was concluded that the following reaction must occur:

$$H_2O_2 + h\nu \longrightarrow OH(^2P) + OH(^2S)$$

For wave-lengths between 2200 and 3000A, there was favored the reaction

$$H_2O_2 + h\nu \longrightarrow OH(^2P_{1/2}) + OH(^2P_{3/2}).$$

Sharma,[107] however, states that reduction of cupric oxide on irradiation in an absorption tube with hydrogen peroxide indicates the formation of atomic hydrogen (process b).

A mixture of 1 per cent hydrogen peroxide in carbon monoxide when circulated at 40° past a quartz window transmitting the wave-lengths 2070 and 2530A produced carbon dioxide by a slow reaction.[108]

When the carbon monoxide was replaced by hydrogen, water was formed. It was assumed that there was a primary decomposition of the peroxide into two hydroxyl radicals which then reacted slowly according to the mechanism proposed by Bonhoeffer and Haber[109] and by Lavin and Jackson.[110]

$$OH + H_2 \longrightarrow H_2O + H$$
$$OH + CO \longrightarrow CO_2 + H.$$

Had the photodissociation of the peroxide yielded instead water and an oxygen atom (process c), no interaction with hydrogen or carbon monoxide should have been observed, since the oxygen atoms would be expected to react much faster with hydrogen peroxide than with hydrogen or carbon monoxide. The reaction

[105] Norrish, R. G. W., and Griffiths, J. G. A., *Proc. Roy. Soc.*, **139A**, 147 (1933); Miyanishi, M., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **27**, 47 (1935); *Chem. Abs.*, **29**, 5351 (1935).

[106] Urey, H. C., Dawsey, L. H., and Rice, F. O., *J. Am. Chem. Soc.*, **51**, 1371 (1929). See also Fergusson, W. C., Slotin, L., and Style, D. W. G., *Trans. Faraday Soc.*, **32**, 956 (1936).

[107] Sharma, R. S., *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 51 (1934); *Chem. Abs.*, **29**, 7187 (1935).

[108] v. Elbe, G., *J. Am. Chem. Soc.*, **54**, 822 (1932); **55**, 62 (1933).

[109] Bonhoeffer, K. F., and Haber, F., *Z. physik. Chem.*, **137A**, 263 (1928).

[110] Lavin, G. I., and Jackson, W. F., *J. Am. Chem. Soc.*, **53**, 383, 3189 (1931).

between OH and H_2 was considered to require an activation energy of not less than 14 kcal. This would keep the rate sufficiently small at temperatures below about 400° to make the predominant reaction

$$OH + OH + M \longrightarrow H_2O_2 + M.$$

But from consideration of the data obtained at various partial pressures and temperatures it was believed that this last reaction ought to be excluded. Accordingly, the results were regarded by v. Elbe as not sustaining the reaction scheme proposed for the mercury-sensitized hydrogen-oxygen reaction by Frankenburger and Klinkhardt which involved the recombination of 2OH to H_2O_2.[111]

The Photo-Oxidation of Hydrogen Iodide. Bates and Lavin[112] studied this reaction at pressures of 50-100 mm. of hydrogen iodide and 150-500 mm. of oxygen at 0°C. Their results led to the conclusion that the quasi-molecule HO_2 may have a life of 10^{-8} or 10^{-9} second, much longer than is usually assigned to such complexes. Kondrat'ev, Kondrat'eva and Lauris[113] studied the effects of irradiating various mixtures of hydrogen iodide and oxygen both in Uviol apparatus transmitting only wave-lengths longer than 2800A and in a quartz apparatus. A larger proportion of the hydrogen iodide was oxidized under the latter conditions. To explain the difference they assumed that in quartz along with the reaction $H + O_2 \longrightarrow HO_2$ there occurs the reaction $H + O_2 \longrightarrow OH + O$. Otherwise the results could be explained by assuming that the probability of occurrence of the reaction $H + O_2 \longrightarrow HO_2$ increases with an increase in the kinetic energies of the hydrogen atoms and oxygen molecules.

Bodenstein and Schenk[114] pointed out that the results of Bates and Lavin might be explained equally well on the assumption that the reaction between H and O_2 occurs as either two-body or three-body collisions. Kinetic studies by Cook and Bates[115] indicated the reaction to be of the latter type, the third body being chiefly either oxygen or hydrogen iodide molecules. The presence of an inert gas such as nitrogen speeds up the reaction. In similar experiments, it was shown that deuterium iodide is always more completely oxidized than is hydrogen iodide.

Winther[116] studied the rate of oxidation of hydriodic acid in the light and in the dark in various solvents.

Photochemical Reactions of the Oxides of Chlorine

Chlorine Monoxide. Balard, the discoverer of chlorine monoxide, observed its decomposition in light into chlorine and oxygen.[117] Bodenstein and Kistiakowsky[118] found that one absorbed quantum (4050 or 4360A) caused the decomposition of two molecules of the monoxide, whether the quantum was absorbed by chlorine monoxide or by some chlorine also present. The reaction was unaf-

[111] Frankenburger, W., and Klinkhardt, H., *Trans. Faraday Soc.*, **27**, 431 (1931); *Z. physik. Chem.* **15B**, 421 (1932).

[112] Bates, J. R., and Lavin, G. I., *J. Am. Chem. Soc.*, **55**, 81, (1933).

[113] Kondrat'ev, V., Kondrat'eva, E., and Lauris, A., *J. Phys. Chem. (U.S.S.R.)*, **5**, 1411 (1934); *Chem. Abs.*, **29**, 7810 (1935).

[114] Bodenstein, M., and Schenk, P. W., *Z. physik. Chem.*, **20B**, 420 (1933).

[115] Cook, G. A., and Bates, J. R., *J. Am. Chem. Soc.*, **57**, 1775 (1935); see also Kistiakowsky, G. B., and Smith, H. A., *Ibid.*, **57**, 835 (1935).

[116] Winther, C., *Z. physik. Chem.*, **113**, 275 (1924); **3B**, 299, 315 (1929); see also Plotnikow, I., *Ibid.*, **111**, 171 (1924).

[117] Balard, A., *Ann. Pharm.*, **14**, 167, 298 (1835).

[118] Bodenstein, M., and Kistiakowsky, G. B., *Z. physik. Chem.*, **116**, 371 (1925).

fected by the presence of air and the temperature coefficient was 1.09. Small amounts of chlorine dioxide were formed during the decomposition. Schumacher and Wagner[119] proposed a mechanism for the reaction in which ClO appears as an intermediate product.

The absorption spectrum of chlorine monoxide is continuous from 2200 to 8500A, so that dissociation is implied. The extinction coefficients have different values in various wave-length regions. Attempts have been made to assign different dissociation processes to different wave-length regions.[120]

Goodeve and Wallace considered three types of dissociation, yielding respectively, Cl_2 and O, ClO and Cl, and Cl, Cl and O. Finkelnburg, Schumacher and Stieger, however, disregard the first possibility and believe that the absorption beginning at 6600A corresponds to the second of these possibilities of dissociation, the chlorine atom probably being excited. Maxima apparent at 5300 and at 4100A were attributed to the same dissociation products but in different states of excitation. Both groups of workers attribute the maximum at 2560A to dissociation into an oxygen atom and two chlorine atoms.

For the wave-lengths 436, 365 and 313 mμ, the rate of decomposition is proportional to the amount of light absorbed, and therefore, independent of the chlorine pressure and also of the Cl_2O pressure until the latter falls below a certain limit. Finkelnburg, Schumacher and Stieger found a higher value than Bodenstein and Kistiakowsky for the quantum yield. It was about 3.5 and varied by only 10 per cent between the extreme wave-lengths. The temperature coefficient, (1.1 in agreement with Bodenstein and Kistiakowsky), increases as the temperature rises. The chain reaction observed was accounted for by the following processes:

$$Cl_2O + h\nu \longrightarrow ClO + Cl \qquad (1)$$
$$Cl + Cl_2O \longrightarrow Cl_2 + ClO \qquad (2)$$
$$ClO + Cl_2O \longrightarrow Cl_2 + O_2 + Cl \qquad (3)$$

Other intermediate products were noted to be ClO_2 and a brown higher oxide of chlorine of unknown composition. A smaller quantum yield observed when the reaction is conducted in solution in carbon tetrachloride[121] was explained by Finkelnburg, Schumacher and Stieger on the assumption that the recombination reactions

$$Cl + Cl \longrightarrow Cl_2$$
$$Cl + ClO \longrightarrow Cl_2O$$

occur so much more frequently in the solution than in the gaseous state that they compete effectively with reaction (2).

The use of shorter wave-lengths (2350-2750A) increases the quantum yield to 4.5 at 20°C.[122] The addition of hydrogen accelerates the decomposition, at least up to the stage at which the secondary reaction, $H_2 + Cl_2 \rightarrow 2HCl$, becomes prominent.[123] Chlorine and oxygen are the main products. Hydrogen atoms are not as important as the ClO radical in continuing the chain, when the pressures of Cl_2O and H_2 are comparable.

The decomposition of chlorine monoxide can be effected by the 5460A line

[119] Schumacher, H. J., and Wagner, C., *Z. physik. Chem.*, **5B**, 199 (1929).
[120] Goodeve, C. F., and Wallace, J., *Trans. Faraday Soc.*, **26**, 254 (1930); Finkelnburg, W., Schumacher, H. J., and Stieger, G., *Z. physik. Chem.*, **15B**, 127 (1931).
[121] Dickinson, R. G., and Jeffreys, C. E. P., *J. Am. Chem. Soc.*, **52**, 4288 (1930).
[122] Schumacher, H. J., and Townend, R. V., *Z. physik. Chem.*, **20B**, 375 (1933).
[123] Iredale, T., and Edwards, T. G., *J. Am. Chem. Soc.*, **59**, 761 (1937).

in the presence of bromine as photosensitizer; under these conditions, the quantum yield is 4.3.[124]

Chlorine Dioxide. Absorption bands of chlorine dioxide, beginning in the blue and violet regions[125] and extending to about 2700A, exhibit rotational fine structure only on the low-frequency side of 3750A.[126] At this point they begin to become diffuse because of predissociation. Schumacher believes a normal oxygen and ClO radical are produced and that at wave-lengths shorter than the convergence limit (2650A by extrapolation), the O atom is liberated in the excited state (^1D). Bowen reported the photodecomposition of the dioxide[127] to produce chlorine, oxygen and Cl_2O_6. Spinks, who secured similar products,[128] found light in the blue and ultraviolet regions equally effective for photodecomposition. Since chlorine dioxide does not absorb at 5460A, this wave-length is ineffective photochemically, except in the presence of bromine when a sensitized reaction occurs with a quantum efficiency practically equal to that produced by the 3650A line.

In later studies,[129] it was shown that in the presence of moisture the reaction is more regular than in the case of the dry gas. The quantum efficiencies for the moist gas are 3.7 at 3650A (predissociation region) and 3.1 at 4360A (excited molecule region). No atomic chlorine is formed. For low concentrations of chlorine dioxide the yield is independent of concentration and light intensity. In dry gas at 17°, the pressure decreases as Cl_2O_6 is formed and condenses on the walls.[130] The reaction is sensitive to temperature changes. At 30°, the pressure increases owing to the decomposition of Cl_2O_6 which yields chlorine and oxygen. In aqueous solutions, at concentrations of chlorine dioxide below 8 per cent, the rate of decomposition is proportional to the light intensity. In the solution there can be detected hypochlorite, chlorate and perchlorate ions.

Photochemical Reactions of Carbon Compounds

Photolysis of Carbon Dioxide. A 15-mm. layer of carbon dioxide at atmospheric pressure exhibits a series of absorption bands beginning at about 1710A (or somewhat longer wave-lengths); these apparently are superposed upon a continuum, possibly indicative of dissociation into carbon monoxide and oxygen.[131] Chapman, Chadwick and Ramsbottom[132] showed that after long intermittent illumination, dry carbon dioxide at atmospheric pressure was decomposed to the extent of 2.6 to 3 per cent. This decomposition was estimated by determining the ratio of carbon monoxide to carbon dioxide in the resulting gases. The oxygen was partially ozonized. When very carefully dried carbon dioxide was used, it was claimed that as much as 46 per cent could be decomposed in 45 hours. No decomposition whatever could be detected as a result of the irradiation of moist gas.

[124] Brown, A. G., and Spinks, J. W. T., *Canadian J. Research*, **15B**, 113 (1937).
[125] Mayer, H., *Z. physik. Chem.*, **113**, 220 (1924); Goodeve, C. F., and Stein, N. O., *Trans. Faraday Soc.*, **25**, 738 (1929); Goodeve, C. F., and Wallace, J., *Ibid.*, **26**, 259 (1930); Ku, Z. W., *Phys. Rev.*, **44**, 376 (1933).
[126] Urey, H. C., and Johnston, H., *Phys. Rev.*, **38**, 2131 (1931); Schumacher, H. J., and Finkelnburg, W., *Z. physik. Chem. Bodenstein Band*, 704 (1931).
[127] Bowen, E. J., *J. Chem. Soc.*, **123**, 2328 (1923); Booth, H., and Bowen, E. J., *J. Chem. Soc.*, **127**, 510 (1925).
[128] Spinks, J. W. T., *J. Am. Chem. Soc.*, **54**, 1689 (1932); **55**, 428 (1933).
[129] Spinks, J. W. T., and Porter, J. M., *J. Am. Chem. Soc.*, **56**, 264 (1934).
[130] See also Bodenstein, M., Harteck, P., and Padelt, E., *Z. anorg. Chem.*, **147**, 233 (1925).
[131] Leifson, S. W., *Astrophys. J.*, **63**, 82 (1926).
[132] Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., *J. Chem. Soc.*, **91**, 942 (1907); **89** 22 (1906).

The effect of water upon the reaction was verified by Coehn and Sieper.[133] The water underwent no change and neither formic acid nor formaldehyde was formed. It was also observed that the photolysis of dry carbon dioxide by radiations shorter than 2540A occurs at a rate inversely proportional to the pressure. A final stationary state is eventually reached. These authors claimed also that some formaldehyde is produced during the irradiation of a mixture of equal volumes of carbon dioxide and hydrogen.

More recently, Coehn and Spitta[134] confirmed and extended the observations on the effect of water upon photolysis of carbon dioxide. They concluded that optimum decomposition at a pressure of 300 mm. occurs in the presence of a very small proportion of water; the addition of larger quantities of moisture or further drying was believed to reduce the decomposition. These conclusions were based upon the observation that 1 per cent decomposition occurred in a sample dried over sulfuric acid, but that a gas which had been in prolonged contact with phosphorus pentoxide was not altered on irradiation. Drying by liquid air reduced the decomposition to 1 per cent but in this gas the addition of a very small quantity of moisture and subsequent ultraviolet irradiation produced a decomposition of 10.5 per cent. Coehn and May[135] have more recently confirmed the inability of ultraviolet light to cause a decomposition in extremely dry carbon dioxide. The xenon lamp decomposes carbon dioxide with a quantum yield of 0.98.[136]

It has been stated by Zenghalis[137] that the reduction of carbon dioxide in aqueous solution by very finely divided hydrogen takes place very slowly in the dark, but is markedly accelerated by sunlight and still more so by ultraviolet rays. In all cases the formaldehyde first produced undergoes polymerization.[137a]

Carbon Monoxide. Although the band spectrum of this gas has been much studied, its complexities are of little photochemical significance.[138] A series of bands extends from about 2064.5A to 920A. The absorption is but slight at wavelengths longer than 1546A. No continuous region is recorded since the heat of dissociation into normal atoms is too great for this process to occur in any readily available spectral region. There may be a predissociation limit at 1063A. Harteck, Groth and Faltings[139] find irradiation with the line 1295A (but not with 1470A) leads to the formation of carbon dioxide and carbon suboxide.

Thiele[140] observed that carbon monoxide and oxygen unite less readily under ultraviolet irradiation than do hydrogen and oxygen. Coehn and Tramm[141] reported that the presence of moisture has no effect on union of carbon monoxide and oxygen. Exposure of moist and various dried mixtures to the radiations from a quartz mercury arc led to practically the same result, combination occurring to the extent of 4 or 5 per cent within an hour. There was, however, some effect of moisture upon the degree of explosibility of the gas mixtures when treated by a spark. A moist mixture could be exploded by a spark at any pressure. A

[133] Coehn, A., and Sieper, G., *Z. physik. Chem.*, **91**, 347 (1916).
[134] Coehn, A., and Spitta, T., *Z. physik. Chem.*, **9B**, 401 (1930).
[135] Coehn, A., and May, B. W., *Z. physik. Chem.*, **26B**, 117 (1934).
[136] Groth, W., *Z. physik. Chem.*, **37B**, 307, 315 (1937).
[137] Zenghalis, C. D., *Compt. rend.*, **171**, 167 (1920); *J. Soc. Chem. Ind.*, **39**, 596A (1920).
[137a] For the sensitized reaction between carbon dioxide and water, see Chapter 43.
[138] Birge, R. T., and Hopfield, J. J., *Phys. Rev.*, **29**, 922 (1927); Leifson, S. W., *Astrophys. J.*, **63**, 82 (1926); Duffendack, O. S., and Fox, G. W., *Nature*, **118**, 12 (1926); Johnson, R. C., *Nature*, **118**, 50 (1926); Coster, D., and Brons, F., *Physica*, **1**, 155 (1934); Schmid, R., *Physik. Z.*, **37**, 55 (1936).
[139] Harteck, P., Groth, W., and Faltings, K., *Z. Elektrochem.*, **44**, 621 (1938).
[140] Thiele, H., *Z. angew. Chem.*, **22**, 2472 (1909).
[141] Coehn, A., and Tramm, H., *Ber.*, **54**, 1148 (1921).

mixture dried by short exposure to solid carbon dioxide and alcohol could not be exploded, but burned quietly. A mixture which had been cooled for a sufficient time could not be ignited, although a pale bluish zone appeared around the spark gap and slight combination was indicated by a small diminution in pressure.

An increase in the temperature coefficient with temperature was observed by Kistiakowsky.[142] This report and the fact that the gas mixture can be made to explode suggested to Jackson[143] that chain reactions are set up. The lack of absorption by carbon monoxide requires that the reaction produced by the 1720A line group of aluminum be explained by a primary dissociation of oxygen molecules. Since the yield of ozone was found to be about the same in mixtures of oxygen with either carbon monoxide or nitrogen, Jackson concluded that the efficiency of the process $O + CO \rightarrow CO_2$ must be at least 150 times lower than that of the reaction $O + O_2 \rightarrow O_3$. The activation energy of the first reaction is at least 3 kcal. greater than that of the latter, providing the steric factors influencing the efficiency of the collisions are the same in both cases. Harteck and Kopsch[144] have reported a similar unreactivity of oxygen atoms (from a discharge tube) toward carbon monoxide.

At high temperatures (500-550°C.), the dry oxidation of carbon monoxide is practically independent of temperature and total pressure. When water is present, the rate depends on the total pressure and has a large temperature coefficient. In the presence of water, the following chain may be set up, according to Jackson,

$$O + H_2O \longrightarrow OH + OH$$
$$OH + CO \longrightarrow CO_2 + H$$
$$H + O_2 + CO \longrightarrow CO_2 + OH.$$

The last two reactions had been suggested by Farkas, Haber and Harteck[145] to explain the photosensitizing action of ammonia in the oxidation of carbon monoxide. The primary photodissociation of the ammonia produces NH_2 and a hydrogen atom, the latter starting the last reaction. It has subsequently been found by Jackson[146] that at high temperatures, hydrogen peroxide is also formed in the presence of moisture.[147]

Popov[148] studied the oxidation of carbon monoxide at pressures as low as 0.01-1.5 mm. of mercury and at temperatures up to 150°. He found the reaction of carbon monoxide and atomic oxygen to be heterogeneous and to have a very small energy of activation. Contrary to the case of the oxidation of carbon monoxide by atomic oxygen obtained by means of a discharge, the efficiency of wall collisions was found to be large. This efficiency could be explained by assuming the participation of metastable ^1D oxygen atoms, which are obtained along with normal state atoms during the photodissociation of molecular oxygen. The reaction is then $CO_{ads.} + O' \rightarrow CO_2$ for the principal process. A correlation between the constants for the kinetic expression for this reaction and the isotherm of the adsorption of carbon monoxide on quartz could be shown.

[142] Kistiakowsky, G. B., *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).
[143] Jackson, W. F., *J. Am. Chem. Soc.*, **56**, 2631 (1934).
[144] Harteck, P., and Kopsch, U., *Z. physik. Chem.*, **12B**, 327 (1931).
[145] Farkas, L., Haber, F., and Harteck, P., *Naturwiss.*, **18**, 266 (1930); *Z. Elektrochem.*, **36**, 711 (1930).
[146] Jackson, W. F., *J. Am. Chem. Soc.*, **57**, 82 (1935).
[147] It has recently been claimed that the interposition of an oxygen filter does not affect the rate of the reaction, although a carbon monoxide filter decreases it. Ziskin, M., Kondrat'ev, V., and Sushkevitch, T., *J. Phys. Chem. (U.S.S.R.)*, **8**, 281 (1936); *Chem. Abs.*, **31**, 1297 (1937).
[148] Popov, B., *Acta Physicochim. U.R.S.S.*, **3**, 223 (1935); *Chem. Abs.*, **30**, 2109 (1936).

The mercury-sensitized reaction between hydrogen and oxygen, in the presence of carbon monoxide, was studied by Barak and Taylor.[149] With equal concentrations of hydrogen and carbon monoxide, the former is oxidized five times as rapidly as the latter. When the hydrogen to carbon monoxide ratio was five to one, 20 per cent of the carbon monoxide formed formaldehyde. Reaction between hydrogen and carbon monoxide occurred at 18 per cent of the rate of that between hydrogen and oxygen in electrolytic gas. These results are consistent with an initial exclusive formation of hydrogen peroxide and a chain reaction with a mean chain-length of approximately six. In similar work, Farkas and Sachsse[150] found hydrogen atoms to combine with carbon monoxide molecules in three-body collisions to yield HCO. If the back reaction takes place and 0.1 of the three-body collisions are effective in the formation of the radical, the ratio of formation to decomposition at room temperatures is 1/370.

The phosgene-sensitized oxidation of carbon monoxide by the unfiltered radiations of the mercury arc has been investigated by Rollefson and Montgomery.[151] They gave the rate expression for low oxygen pressures as

$$\frac{d(CO_2)}{dt} = k\sqrt{I_0[COCl_2][CO][O_2]}$$

At higher oxygen pressures, the rate becomes independent of the oxygen pressure. These authors suggested that the mechanism of this reaction is very similar to that of the chlorine-sensitized reaction.[152]

The latter is quite complicated, a thousand molecules of carbon dioxide per quantum being formed in mixtures of a half atmosphere each of chlorine, carbon monoxide and oxygen. In blue light at high pressures and in large vessels, the rate of production of carbon dioxide is proportional to the chlorine concentrations and to the square root of that of carbon monoxide. For small pressures and vessels with a large surface, it is proportional to the square root of the concentrations of carbon monoxide and chlorine.

In the presence of nitric oxide, a small proportion of the carbon monoxide present is, on irradiation by ultraviolet rays, converted into carbon dioxide by interaction with oxygen liberated from the nitric oxide.[153]

In the decomposition of carbon monoxide in the silent electric discharge a brown solid not identical with polymerized carbon suboxide is formed.[154]

The Photochemistry of Phosgene

Formation of Phosgene. The formation of phosgene from carbon monoxide and chlorine, reported by Davy in 1812,[155] is somewhat analogous to the combination of hydrogen and chlorine in that the reaction has a very high quantum yield, is under certain conditions inhibited by oxygen and is to a high degree subject to the influence of traces of impurities which give rise to induction periods.[156]

[149] Barak, M., and Taylor, H. S., *Trans. Faraday Soc.*, **28,** 569 (1932); for early observations see Herchefinkel, H., *Compt. rend.*, **149,** 395 (1909). See also page 257.

[150] Farkas, L., and Sachsse, H., *Z. physik. Chem.*, **27B,** 111 (1934).

[151] Rollefson, G. K., and Montgomery, C. W., *J. Am. Chem. Soc.*, **55,** 4036 (1933).

[152] For a full discussion of the reaction schemes proposed for the latter, see Schumacher, H. J., and Stieger, G., [*Z. physik. Chem.*, **13B,** 157 (1931)]; Warming, E., [*Z. physik. Chem.*, **18B,** 153 (1932)]; Schumacher, H. J., [*Z. physik. Chem.*, **18B,** 155 (1932)]; and Franke, W. K., and Schumacher, H. J., [*Ibid.*, **B40,** 115 (1938)].

[153] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **157,** 129 (1913).

[154] Crespi, M., and Lunt, R. W., *J. Chem. Soc.*, **127,** 2052 (1925); Lunt, R. W., and Mumford, L. S., *J. Chem. Soc.*, 1711 (**1929**).

[155] Davy, H., *Phil. Trans.*, **30,** 144 (1812).

Details of the kinetics of this reaction were reported by Bodenstein.[157] The results with various mixtures of carbon monoxide and chlorine were complicated and for a considerable time considered to be affected by traces of moisture present. It was established that oxygen retards the reaction until near completion of the latter, when its effect suddenly decreases. The oxygen is consumed by a chlorine-sensitized reaction in which carbon monoxide is oxidized to the dioxide. Carbon dioxide formation is proportional to the carbon monoxide pressure, increases with the chlorine pressure, but more slowly than in direct proportion, and decreases with increasing oxygen concentration, but not so rapidly as to be inversely proportional to the latter. At room temperature, the rate of formation of phosgene was found to be proportional to the chlorine concentration, to the square root of the absorbed energy and to the square root of the carbon monoxide concentration. The temperature coefficient near room temperature is unity or slightly less.

Subsequent work by Bodenstein and Onoda[158] revealed that the order of reaction is different at temperatures between 200° and 300°C. The rate of formation of the phosgene is then directly proportional to the absorbed energy, and to the concentrations of the reactants (chlorine and carbon monoxide). At these temperatures, furthermore, the retarding effect of oxygen is no longer observable. At 300°C. no formation of carbon dioxide occurs in the presence of oxygen. Between 270° and 300°C., the velocity coefficient is considerably influenced by hydrolysis of phosgene by water vapor, but at the higher temperatures all the water vapor appears to be removed in the early stages of the reaction. A poisoning effect of small quantities of carbon dioxide in the reaction at ordinary temperatures was demonstrated by Cathala.[159] The effect is diminished when wavelengths shorter than 3500A are employed in the irradiation.

As in the case of the hydrogen-bromine reaction, a mechanism to account for the kinetics of the reaction was developed by Bodenstein[160] by extending the mechanism used to account for the thermal reaction. The result was a succession of processes which involved excited chlorine and carbon monoxide molecules, as well as the chlorine atoms and triatomic chlorine molecules which are assumed to play a part in the thermal process. Although the introduction of a few assumptions regarding the rate constants of the partial reactions permitted a fairly satisfactory derivation of an expression similar to the experimental rate expression, the Bodenstein formulation has since been superseded by others which avoid the assumption of excited chlorine molecules as the products of the primary process.

A primary photodissociation of chlorine molecules was made the first step in the formulation of Bodenstein, Lenher and Wagner[161] which was based on an investigation of the reaction at low total pressures (below 40 mm.) and at ordinary temperatures. The partial reactions proposed were the following:

[156] Chapman, D. L., and Gee, F. H., *J. Chem. Soc.*, **99,** 1726 (1911); Dyson, G., and Harden, A., *J. Chem. Soc.*, **83,** 201 (1903). For a general review, see Kistiakowsky, G. B., *Z. angew. Chem.*, **44,** 602 (1931). Early kinetic measurements were reported by Wildermann, M., *Phil. Trans.*, **199A,** 337 (1902); *Z. physik. Chem.*, **42,** 257 (1903).

[157] Bodenstein, M., *Rec. trav. Chim.*, **41,** 585 (1922).

[158] Bodenstein, M., and Onoda, T., *Z. physik. Chem.*, **131,** 153 (1928).

[159] Cathala, J., *J. chim. phys.*, **24,** 663 (1927).

[160] Bodenstein, M., *Sitzb. Preuss. Akad.*, **13,** 104 (1926); *Z. physik. Chem.*, **130,** 422 (1927); Schumacher, H. J., *Z. physik. Chem.*, 129, 241 (1927).

[161] Bodenstein, M., Lenher, S., and Wagner, C., *Z. physik. Chem.*, **3B,** 459 (1929).

(1) $Cl_2 + h\nu \longrightarrow 2Cl$
(2) $CO + Cl \longrightarrow COCl$
(3) $COCl \longrightarrow CO + Cl$
(4) $CO + Cl_2 + Cl \longrightarrow COCl_2 + Cl$
(5) $COCl + Cl \longrightarrow CO + Cl_2$
(6) $COCl + O_2 \longrightarrow CO_2 + ClO$
(7) $ClO + CO \longrightarrow CO_2 + Cl.$

The last two reactions were employed only to account for the inhibiting action of oxygen and the sensitized formation of carbon dioxide. In this scheme there is supposed to be an equilibrium between the hypothetical COCl molecule and its decomposition products. The phosgene is formed only by the triple collisions in (4); it is to be noted that (4) is a chain reaction and accounts for the high quantum yield. By making the formation of phosgene depend upon a reaction involving triple collisions, the slowness of reaction at low pressures could be accounted for. In addition to processes (2) and (5), which represent removal of chlorine atoms in the gas phase, both COCl and Cl diffuse to the walls of the vessel where recombination occurs. Processes involving water were not included since Schultze [162] found the previously much-discussed effect of traces of moisture to be non-existent. By a treatment of these partial reactions in a manner analogous to that discussed in the section on hydrogen bromide, it can be shown that the rate constant is (as experimentally found) a function of the square root of the intensity of the light.

Lenher and Rollefson,[163] however, objected to the assumption of an equilibrium between COCl and CO and Cl on the ground that the hypothetical intermediate should be expected to react with chlorine as well as with oxygen. They assumed the phosgene to be formed by the process $COCl + Cl_2 \rightarrow COCl_2 + Cl$. Furthermore, the formation of the intermediate was believed to occur through a triple collision: $CO + Cl + M \rightarrow COCl$, in which chlorine molecules may function as the inert molecule with a relatively high efficiency. The rate of formation of phosgene was believed to be so fast compared to the rate of decomposition of COCl that the former may be considered the determining factor in fixing the concentration of the intermediate.

To account for the change in reaction order at 300°C. observed by Schumacher,[164] Lenher and Rollefson consider that the decomposition of COCl into Cl and CO is very rapid at this temperature. The equilibrium concentration of this intermediate (COCl) is very small, under which condition the chain-breaking reactions (6) and (7) have very small rates. The low steady state of COCl makes it necessary to assume for the formation of the phosgene reaction (4) of the Bodenstein, Lenher and Wagner mechanism. At room temperatures, reaction (4) is supposed to be subordinate to the process: $COCl + Cl_2 \rightarrow COCl_2 + Cl$. At high temperatures, chlorine atoms can only be removed by recombination at the wall or by collisions in the gas phase, rather than by combination with COCl. Therefore, the concentration of chlorine atoms becomes sufficient to permit of the formation of phosgene by the Bodenstein reaction. Schumacher and Stieger [165] showed that at temperatures above 250°C. and also at room temperatures when the total pressures were below one atmosphere or the vessels used had relatively large

[162] Schultze, G., *Z. physik. Chem.*, **5B**, 368 (1929).
[163] Lenher, S., and Rollefson, G. K., *J. Am. Chem. Soc.*, **52**, 500 (1930).
[164] Schumacher, H. J., *Z. physik. Chem.*, **129**, 241 (1927).
[165] Schumacher, H. J., and Stieger, G., *Z. physik. Chem.*, **13B**, 157 (1931).

surfaces, a considerable portion of the chlorine atoms recombine on the walls of the vessel. The new mechanism is adequate to describe the rate of formation of phosgene under these conditions.

Schumacher,[166] as well as Warming,[167] however, defended the mechanism of Bodenstein, Lenher and Wagner. They believe the rate of formation of COCl by triple collisions to be reasonably fast at ordinary pressures and state that the heat of formation of this molecule is so low that the decomposition must proceed at a rapid rate. Rollefson [168] asserts that it is impossible for COCl to attain its equilibrium concentration since other reactions, for example, between Cl_2 and COCl, occur too rapidly. The distinction is that in the Rollefson mechanism the COCl molecule may react either with chlorine or oxygen, the relative amounts of the two being determined by the specific rate constants and the relative pressures of the gases. On the other hand, in the Bodenstein mechanism it was postulated that only the oxygen could react with the COCl. The latter molecule was assumed to be in equilibrium with its dissociation products in the absence of oxygen, but not in its presence. The relative amounts of carbon dioxide and phosgene formed will depend upon the manner in which the COCl molecules divide between the two paths open to them. Increase of the pressure of oxygen at a definite pressure of chlorine should cause a decrease in the amount of phosgene formed and preliminary experiments appeared to indicate this to be the case. Rollefson [169] stated later that the specific rates for the two reactions destroying COCl are of the same order of magnitude. The phosgene formation has a higher temperature coefficient and therefore higher energy of activation than that leading to the formation of carbon dioxide. The relative amounts of the two reactions is a function solely of the ratio of chlorine to oxygen at constant temperature.

In a more recent paper, however, Rollefson [170] concludes that the active form of chlorine involved in the chain process is probably triatomic chlorine and believes the intermediate to be formed by

$$CO + Cl_3 \longrightarrow COCl + Cl_2.^{171}$$

Recently, the reaction has been restudied by Bodenstein, Brenschede and Schumacher,[172] using very pure gases over a wide concentration range. The mercury line 4358A was used for the reaction at 14-16°C., pressure measurements being made with a quartz spiral manometer. Evidence was given to show that COCl rather than Cl_3 is the intermediate at chlorine pressures between 340 and 180 mm. Below this and down to 15 mm., there was evidence for an additional chain-breaking mechanism $H + COCl_2 \rightarrow HCl + COCl$ on the wall, and another method of phosgene formation. Also,[173] they have investigated the induction and after-periods by a rotating sector method, and found the resulting rate changes in agreement with those calculated from their mechanism. If the gases were not free from oxygen, the after-effects were five times as large. Oxygen inhibits the

[166] Schumacher, H. J., *J. Am. Chem. Soc.*, **52**, 3132 (1930).
[167] Warming, E., *Z. physik. Chem.*, **18B**, 156 (1932).
[168] Rollefson, G. K., *Trans. Faraday Soc.*, **27**, 465 (1931).
[169] Rollefson, G. K., *J. Am. Chem. Soc.*, **55**, 148 (1933).
[170] Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 579 (1934); see also Rollefson, G. K., and Eyring, H., *J. Am. Chem. Soc.*, **54**, 170 (1932); Rollefson, G. K., *Z. physik. Chem.*, **37B**, 472 (1937).
[171] Cathala, J., *J. chim. phys.*, **25**, 182 (1928) had previously assumed the phosgene to be formed by the reaction: $Cl_3 + CO \rightarrow COCl_2 + Cl$.
[172] Bodenstein, M., Brenschede, W., and Schumacher, H., *Z. physik. Chem.*, **28B**, 81 (1935); **40B**, 121 (1938).
[173] Bodenstein, M., Brenschede, W., and Schumacher, H. J., *Z. physik. Chem.*, **35B**, 382 (1937); See also Taylor, H. S., *J. Phys. Chem.*, **42**, 789 (1938).

stationary formation of phosgene, but does not affect the equilibrium: $COCl \leftrightarrows CO + Cl$. This indicates the possible presence of an oxygen-containing intermediate compound with a longer life than either Cl or COCl.

The photochemical formation of phosgene from chloroform and oxygen (sensitized by chlorine) has been found to occur by Schumacher and Wolff.[174] The following mechanism is proposed:

$$(1) \quad Cl_2 + h\nu \longrightarrow 2Cl$$
$$(2) \quad Cl + CHCl_3 \longrightarrow CCl_3 + HCl$$
$$(3) \quad CCl_3 + O_2 \longrightarrow CCl_3O_2$$

The last compound forms phosgene and also breaks the chains. The quantum yield at 65° and a chloroform pressure of 100 mm. is 260 moles per einstein. The chain-breaking process can be neither a three-body collision nor diffusion to the walls since the rate is independent of the pressure. It is proportional to the absorbed light and to the square root of the chloroform concentration. The temperature coefficient is 1.23. The reaction is not influenced by hydrogen chloride or phosgene. It is almost completely inhibited by alcohols or ammonia, these substances being chlorinated and then decomposing. Completely chlorinated substances do not inhibit the reaction.[175]

Decomposition of Phosgene. Absorption data by Henri and Howell[176] indicated a region of absorption bands of phosgene to begin at 3041A. The bands become diffuse at 2750A and extend to 2380A beyond which the absorption becomes continuous. When phosgene is heated to 100-200°C., an additional continuous spectrum overlays the bands.

Weigert[177] found irradiation of phosgene at 500°C. caused no displacement from the thermal equilibrium ratio of the gas and its decomposition products, and in this Bodenstein and Onoda[178] concur. At the ordinary temperatures, phosgene, passed through a quartz tube at the rate of 1 cc. per minute, was decomposed to the extent of 3.3 to 4 per cent.[179] In a Uviol tube permeable only to radiations of wave-length longer than 2650A, the decomposition reached only 0.46-0.5 per cent. In ordinary glass tubes there was no decomposition. In each case the equilibrium could be approached from either side.

Almasy and Wagner-Jauregg[180] studied the decomposition of phosgene at 300 mm. pressure at both 20° and 160°C. in a quartz vessel surrounded by a mercury arc lamp. For isolating the region of bands a filter of 5 per cent benzene in hexane was used. To eliminate the effect of absorption by the liberated chlorine, the quartz vessel was surrounded by a chlorine filter. The contents of the vessel after irradiation were analyzed by freezing out the chlorine and phosgene and following the pressure change, or by titrating the chlorine and phosgene. The absorption of radiations in the region of sharp bands produced a decomposition to the extent of 0.25 to 1.75 per cent depending on the intensity of the light and the pressure of the phosgene. The decomposition was not increased at 160°C. It was assumed to be due to some process of predissociation and required no more

[174] Schumacher, H. J., and Wolff, K., *Z. physik. Chem.*, **16B**, 453 (1934).
[175] Schumacher, H. J., and Sundhoff, D., *Z. physik. Chem.*, **34B**, 300 (1936).
[176] Henri, V., and Howell, O. R., *Proc. Roy. Soc.*, **128**, 192 (1930).
[177] Weigert, F., *Ann. Physik*, **24**, 55 (1907).
[178] Bodenstein, M., and Onoda, T., *Z. physik. Chem.*, **131**, 153 (1928).
[179] Coehn, A., and Becker, H., *Ber.*, **43**, 130 (1910).
[180] Almasy, F., and Wagner-Jauregg, T., *Naturwiss.*, **19**, 270 (1931); *Z. physik. Chem.*, **19B**, 405 (1932).

than 100 kcal. The use of the entire mercury arc spectrum increased the decomposition to 2.19 to 8.65 per cent. Under these conditions the decomposition was nearly doubled at 160°C. Rollefson and Montgomery,[181] found that in the presence of oxygen, the rate of formation of carbon dioxide was directly proportional to the phosgene concentration and to the incident light intensity at either 20°, 90° or 200°C. At higher oxygen pressures, the rate was independent of the oxygen concentration, but at lower pressures it gradually fell off with decreasing oxygen, the rate being a function of the chlorine-oxygen ratio rather than of the oxygen concentration itself. They derived the rate law

$$\frac{d(CO_2)}{dt} = \frac{kI_0(COCl_2)}{1 + k'\left(\frac{Cl_2}{O_2}\right)}$$

from the following series of reactions.

$$(1) \quad COCl_2 + h\nu \longrightarrow COCl + Cl$$
$$(2) \quad COCl + O_2 \longrightarrow CO_2 + ClO$$
$$(3) \quad COCl_2 + ClO \longrightarrow CO_2 + Cl_2 + Cl$$
$$(4) \quad COCl + Cl_2 \longrightarrow COCl_2 + Cl$$
$$(5) \quad Cl + M \longrightarrow 1/2Cl_2 + M$$
$$(6) \quad Cl + Cl \longrightarrow Cl_2$$

From the derivation it is apparent that the value of k' in the rate equation expressed the relative reactivity of the COCl molecule with chlorine and with oxygen. The average quantum yield of the decomposition was found to be 1.8. For the phosgene-sensitized oxidation of carbon monoxide they found quantum yields of 90 to 110, lower than those of others cited in the discussion of that reaction.[182]

The exposure of mixtures of phosgene and hydrogen to ultraviolet radiation results in a much greater decomposition, up to 97 per cent, since liberated chlorine may combine with the hydrogen to form hydrogen chloride. Bredig and von Goldberger[183] failed in attempts to obtain formaldehyde according to the reaction: $COCl_2 + 2H_2 \rightarrow CH_2O + 2HCl$. At 10°C., minute traces were obtained, but there was none at all at 80°C. The walls of the reaction vessel were observed to be coated with a white to brown deposit.

Montgomery and Rollefson[184] found the initial rate of the decomposition in the presence of hydrogen to be rather insensitive to a tenfold variation in the pressure of the latter gas, although the initial rate showed a slight increase as the hydrogen pressure was increased. With increase in the phosgene pressure, the rate had an upward trend but appeared to approach a limiting value at high phosgene pressures. By plotting the initial rates against the calculated percentage of absorption of the 2537A line (the most intense line beyond the predissociation limit) a straight line was obtained, indicating the rate to be a function of the first power of the absorbed light, as well as of the incident intensity. There was, however, a deviation from a simple first order law, since the rate of change of the logarithm of the phosgene concentration did not remain constant with time. In seeking the cause of this deviation, it was found that the rate is inversely proportional to, or at least involves a term which is inversely proportional to, the total

[181] Rollefson, G. K., and Montgomery, C. W., *J. Am. Chem. Soc.*, **55**, 142 (1933).
[182] Montgomery, C. W., and Rollefson, G. K., *J. Am. Chem. Soc.*, **55**, 4025 (1933).
[183] Bredig, G., and v. Goldberger, A., *Z. physik. Chem.*, **110**, 521 (1924).
[184] Montgomery, C. W., and Rollefson, G. K., *J. Am. Chem. Soc.*, **55**, 4030 (1933).

pressure as varied by the addition of carbon dioxide or nitrogen. This effect was more pronounced when carbon monoxide was the added gas, in which case there was some evidence that the carbon monoxide concentration enters the rate law explicitly. It appeared likely that the deviation from first order may depend upon the ratio of added hydrogen to added carbon monoxide when both are added.

From the reaction mechanism

$$\begin{aligned}
&(1) \quad COCl_2 + h\nu \longrightarrow COCl + Cl\\
&(2) \quad Cl + H_2 \longrightarrow HCl + H\\
&(3) \quad H + COCl_2 \longrightarrow CO + Cl + HCl\\
&(4) \quad CO + M + Cl \longrightarrow COCl + M\\
&(5) \quad 2COCl \longrightarrow COCl_2 + CO
\end{aligned}$$

it was possible to derive the rate equation

$$\frac{d(CO)}{dt} = I_0(COCl_2)\left[1 + \frac{k_2(H_2)}{k_4(CO)\,(M)}\right]$$

which seemed in agreement with the experimental facts. The second term makes its largest contribution to the rate at the start of the reaction, and the first two or three values of the divergence from a first order reaction are always larger than succeeding values. It also appeared that the quantum yield was 3.7 at two minutes, decreasing to 2.4 at eight minutes. The concentration of M (any molecule capable of taking up the excess energy of COCl and so stabilizing it) was assumed equal to the total pressure. This would be the case if all kinds of molecules present are equally capable of acting in this way, even though carbon monoxide may have a more pronounced effect than nitrogen. The absence of formaldehyde formation was attributed to the non-reactivity of COCl toward hydrogen. This non-reactivity is believed to cause an increase in the concentration of COCl so that reaction (5) becomes the chain-terminating process.

Kassel [185] found an error in the derivation of the rate law in that the rate of production of CO in (5) was erroneously taken as equal to the rate of consumption of COCl in this step. If this is corrected, the 1 within the bracket of the final rate equation drops out and agreement with experiment is lost. Kassel suggested the mechanism:

$$\begin{aligned}
&(3a) \quad H + COCl_2 \longrightarrow HCl + COCl\\
&(5a) \quad 2COCl \longrightarrow 2CO + Cl_2\\
&(7) \quad COCl + Cl_2 \longrightarrow COCl_2 + Cl\\
&(8) \quad COCl + H_2 \longrightarrow CO + HCl + H.
\end{aligned}$$

This leads to the rate equation

$$\frac{d(CO)}{dt} = \frac{2I_{Abs}k_2(H_2)}{k_2(H_2) + k_4(CO)\,(M)} + k_8\sqrt{I_{Abs}/k_{6a}(H_2)}$$

Some work has been done on the photochemistry of bromophosgene. Trautz [186] had stated that the bromo compound could be formed photochemically. However, Schumacher and Bergmann,[187] who irradiated mixtures of carbon monoxide and bromine with different portions of the spectrum, concluded that at temperatures less than 100°C., neither excited bromine molecules nor bromine atoms react with carbon monoxide to form bromophosgene. Furthermore, when mixtures of bromophosgene and bromine were irradiated with light in the absorption band region of bromine, no pressure change was noted. When irradiated in its own absorption region (3200-2100A) bromophosgene is, however, decomposed with a quantum yield of unity. The reaction is of zero order and non-absorbing foreign gases do not affect the rate. The temperature coefficient is one for 10° between 10° and 40°C.

No reaction between carbon monoxide and fluorine could be detected when a mixture of these gases was irradiated in a quartz tube by ultraviolet rays.[188]

[185] Kassel, L. S., *J. Am. Chem. Soc.*, **56**, 243 (1934).
[186] Trautz, M., *Z. Elektrochem.*, **21**, 329 (1915).
[187] Schumacher, H. J., and Bergmann, P., *Z. physik. Chem.*, **13B**, 269 (1931).

The Photochemistry of Nitrogen Compounds

The absorption by nitrogen has been studied by Birge and Hopfield [189] and by Sponer.[190] The spectrum consists of a system of bands beginning at 1450A and extending to 1227A. Excited molecules are formed. No photochemical reactions which can be attributed to this absorption are known as yet.

Ammonia. The ultraviolet absorption of this gas is limited to the region of wave-lengths shorter than about 2200A or 2400A. Between this limit and 1860A is a region of absorption with a maximum at 1910-1935A.[191] This region comprises a series of diffuse predissociation bands, the investigation of which by Bonhoeffer and Farkas [192] gave the first indication that predissociation in general implies a spontaneous decomposition. These workers were unable to observe fluorescence of light absorbed in this region, showing that the molecules excited by absorption did not persist long enough to emit energy spontaneously. By the use of the para-hydrogen method, Geib and Harteck [193] subsequently proved the presence of atomic hydrogen in ammonia which has absorbed radiations within this region.[194] The primary process appears to be a dissociation into NH_2 and H; recombination is rapid, and the concentration of hydrogen atoms is very small. Further spectroscopic evidence for this interpretation was found in the measurements and analysis by Dixon [195] of 16 strong bands between 1900 and 2400A. Duncan [196] has shown that the diffuse predissociation bands continue to 1665A, after which they become sharp and show rotational fine structure. True continuous absorption does not appear until about 1200A. At 1150A and below, the continuous absorption becomes so strong that the superposed sharp bands can no longer be measured accurately; the latter continue, however, at least down to 1085A. Electron impact studies of ammonia at electron accelerations corresponding to wave-lengths within this very short wave-length region have been reported by Waldie,[197] Bartlett,[198] and McLennan and Greenwood [199] but are of little

[188] Humiston, B., *J. Phys. Chem.*, **23**, 572 (1919); *Chem. Abs.*, **14**, 534 (1920).
[189] Birge, R. T., and Hopfield, J. J., *Astrophys. J.*, **68**, 257 (1928); Hopfield, J. J., *Phys. Rev.*, **36**, 789 (1930).
[190] Sponer, H., *Proc. Nat. Acad. Sci.*, **13**, 100 (1927); *Z. Physik*, **41**, 611 (1927).
[191] Landsberg, G., and Predwoditeleff, A., *Z. Physik*, **31**, 544 (1925).
[192] Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **134**, 337 (1928).
[193] Geib, K. H., and Harteck, P., *Z. physik. Chem. Bodenstein Band*, 861 (1931).
[194] Ammonia is also known to sensitize reactions in which atomic hydrogen is required. Farkas, L., Haber, F., and Harteck, P., *Naturwiss.*, **12**, 267 (1930); Taylor, H. S., and Emeléus, H. J., *J. Am. Chem. Soc.*, **53**, 562 (1931).
[195] Dixon, J. K., *Phys. Rev.*, **43**, 711 (1933).
[196] Duncan, A. B. F., *Phys. Rev.*, **47**, 822 (1935).
[197] Waldie, A. T., *J. Frank. Inst.*, **200**, 507 (1925).
[198] Bartlett, J. H., Jr., *Phys. Rev.*, **33**, 169 (1928).
[199] McLennan, J. C., and Greenwood, G., *Proc. Roy. Soc.*, **120A**, 283 (1928).

significance for the photochemistry of ammonia. Experiments on the decomposition of ammonia in discharge tubes [200] have also been indicative of the formation of atomic hydrogen and of some compound of hydrogen and nitrogen, NH_2 or NH.

Chemical evidence for the decomposition of ammonia by ultraviolet light was first advanced by Regener [201] and by Berthelot and Gaudechon.[202] Coehn and Prigent [203] were unable to demonstrate a stationary state. Instead the decomposition appeared to go to completion within six hours. The ammonia was sealed in quartz tubes and irradiated with a quartz mercury arc. No ammonia could be demonstrated in a mixture of nitrogen and hydrogen, with or without chlorine as sensitizer, after irradiation with a quartz mercury arc. Noyes [204] has found ammonia to be formed in small amounts when a mixture of nitrogen, hydrogen and mercury vapor is exposed at the boiling point of mercury to light from a quartz mercury arc. Only traces of hydrazine could be detected. The reaction has been attributed to the dissociation of hydrogen by the excited mercury atom.[205]

The quantum yield of the decomposition of ammonia at room temperature by wave-lengths 2025 to 2041A was found by Warburg [206] to be 0.23-0.25. The rate of the decomposition was not affected by the addition of the decomposition products, even when so much of these were added as to make the ammonia but 5 per cent of the gas mixture. Kuhn [207] found the rate proportional to the incident light intensity, and verified the observation that the quantum yield was independent of the ammonia pressure. The value of the yield was, however, 0.45, nearly twice that of Warburg. The yield could, however, be decreased to 0.10 by using light of only two spectral lines, 2063 and 2100A. At high temperatures (500°C.) the speed of decomposition was nine times as great as at 20°C. The quantum yield increased by about 50 per cent for every 100° increase in temperature, reaching 3.3 at 500°. At this temperature the rate of decomposition could be retarded by the addition of hydrogen, although nitrogen had no effect.

In a repetition of these experiments, Wiig and Kistiakowsky [208] verified the Warburg values for the quantum yield at room temperature, 0.23, zinc spark, mean wave-length, 2090A, 0.24, aluminum spark, mean wave-length, 1962A, 0.25, cadmium spark, mean wave-length, 2144A. At 500°C. the quantum yield increased only to 0.48. They were inclined to attribute Kuhn's high value at 500°C. and his observation of a decrease in quantum yield when the monochromatic nature of the light was increased, to experimental error. They found further that the quantum yield is independent of the ammonia pressure over the range 1 to 800 mm. Also the quantum yield was not affected by seven-fold variations in the intensity of the radiation or of seventeen-fold variations in the extent to which decomposition had occurred when the data were taken for the computations.

The use of radiations transmitted by fluorite but not by quartz increases the

[200] Hutchinson, W. K., and Hinshelwood, C. N., *Proc. Roy. Soc.*, **117A**, 131 (1927); Lavin, G. I., and Bates, J. R., *Nature*, **125**, 709 (1930).

[201] Regener, E., *Preuss. Akad.*, 1228 (**1904**).

[202] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1169, 1327, 1517, 1690 (1910); **155**, 207 (1912); **156**, 124 (1913).

[203] Coehn, A., and Prigent, G., *Z. Elektrochem.*, **20**, 275 (1914).

[204] Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **47**, 1003 (1925).

[205] For the synthesis of ammonia in an arc, see Storch, H. H., and Olson, A. R., *J. Am. Chem. Soc.*, **45**, 1605 (1923); Olson, A. R., *Ibid.*, **48**, 1298 (1926); Mochan, I., Roginskiĭ, S., Fedorov, F., and Shekhter, A., *Compt. rend. acad. sci. (U.R.S.S.)*, **2**, 365 (1934); *Chem. Abs.*, **28**, 5339 (1934).

[206] Warburg, E., *Sitzb. Preuss. Akad.*, 746 (**1911**); 216 (**1912**); 872 (**1914**).

[207] Kuhn, W., *Compt. rend.*, **178** (1924); **177**, 956 (1923); *J. chim. phys.*, **23**, 521 (1926).

[208] Wiig, E. O., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **54**, 1806 (1932).

quantum yield to 0.69, so that the yield appears to be higher in the region 1900-1600A.[209] The xenon lamp, however, gives a quantum yield of but 0.17.[210]

Prior to the work of Bonhoeffer and Farkas on the nature of the predissociation process, evidence was advanced by both Dickinson and Mitchell [211] and Taylor and Bates [212] that was difficult to reconcile with the simple excited molecule mechanisms. These workers showed that the decomposition mixture contained more hydrogen (87-96 per cent) than would correspond to the stoichiometrical relation. This could be interpreted only as indicative of the formation of some hydrazine. Bates and Taylor suggested that excited ammonia molecules might either react with normal molecules to produce hydrazine and ammonia or that they might spontaneously yield atomic hydrogen and NH_2 radicals, the latter then forming hydrazine and atomic hydrogen by reaction with ammonia, or reforming ammonia and atomic hydrogen by reacting with hydrogen molecules.

At present, the NH_2 molecules, which are responsible for the formation of hydrazine, are regarded as arising from the predissociation of ammonia. Not much hydrazine is formed when ammonia is irradiated at room temperatures. Wiig and Kistiakowsky even found the composition of the resulting gases to be the same as that formed in the thermal decomposition, that is, close to a 1:3 nitrogen: hydrogen ratio. Koenig and Brings [213] studied the formation of hydrazine at temperatures of −80°C. in the glow discharge, but found that the yield, referred to the electrical energy consumed, was smaller than that with flowing gas at room temperature. Irradiation by the zinc spark caused not only formation but also decomposition of hydrazine, so that only traces could be obtained. They believed hydrazine to be formed in larger amount by the reaction $NH_3 + NH \rightarrow N_2H_4$ than by direct combination of two NH_2 radicals. Gedye and Rideal [214] claimed the yield could be increased by employing low temperatures, a high rate of gas flow and rapid cooling of the gaseous decomposition products. Under the best conditions and using the entire mercury arc spectrum, the yield of hydrazine was said to amount to 50 per cent of the ammonia decomposed.

Wiig and Kistiakowsky discounted the dissociation of ammonia into NH and H_2, since such dissociation did not lead to a mechanism in agreement with the experimental results.[215] Nor did they believe their failure to observe hydrazine in the ammonia decomposition could be ascribed to its simultaneous photochemical decomposition.[215a] They considered the likelihood of occurrence of each of the following secondary reactions.

(1) $H + H + M \longrightarrow H_2 + M$
(2) $NH_2 + H + M \longrightarrow NH_3 + M$
(3) $NH_2 + H_2 \longrightarrow NH_3 + H$
(4) $NH_3 + H \longrightarrow NH_2 + H_2$
(5) $NH_2 + NH_2 + M \longrightarrow N_2H_4 + M$
(6) $NH_2 + NH_2 \longrightarrow N_2 + 2H_2$
(7) $N_2H_4 + H \longrightarrow N_2H_3 + H_2$
(8) $N_2H_3 + N_2H_3 \longrightarrow 2NH_3 + N_2$

[209] Kassel, L. S., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **49**, 2495 (1927).

[210] Groth, W., *Z. physik. Chem.*, **37B**, 307 (1937).

[211] Dickinson, R. G., and Mitchell, A. G., *Proc. Nat. Acad. Sci.*, **12**, 692 (1926); *J. Am. Chem. Soc.* **49**, 1478 (1927).

[212] Taylor, H. S., and Bates, J. R., *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).

[213] Koenig, A., and Brings, T., *Z. physik. Chem., Bodenstein-Band*, 541 (**1931**).

[214] Gedye, G. R., and Rideal, E. K., *J. Chem. Soc.*, 1160 (**1932**).

[215] Wiig, E. O., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **54**, 1817 (1932).

[215a] See in this connection, the discussion of the photochemical decomposition of hydrazine.

Triple collisions are probably not necessary in reactions (2) and (5).[216] At room temperature, (3) may be neglected as it implies a retardation of the rate of decomposition by hydrogen, an effect observable only at high temperatures. According to Boehm and Bonhoeffer,[217] (4) occurs extremely slowly. It may be that the increase in the quantum yield at high temperatures can be accounted for by this reaction, and that (3) also becomes effective under these conditions. Reactions (7) and (8) were set up to explain the absence of more than traces of hydrazine. The reaction at ordinary temperatures involves, according to Wiig and Kistiakowsky, reactions (1), (2), (5) and (7). The quantum yield on these assumptions would be determined by the ratio k_2^2/k_1k_5, this fraction being required to have a value of eight in order to account for a quantum yield of 0.25.

By using deuterium as an indicator, Taylor and Jungers[218] concluded that reaction (2) occurs to such an extent as to make it one of the reasons for the low quantum yield.[219] By irradiating mixtures of ammonia and deuterium, an equilibrium mixture of NHD_2 and NH_2D were obtained.

Studies of the concentrations[220] of atomic hydrogen produced by the irradiation of ammonia showed that the yields were independent of the total pressure when the latter was varied from 250 to 760 mm. The atomic hydrogen was proportional to the 0.69 power of the absorbed light intensity, and passed through a maximum with increasing ammonia pressure. The effect of changing the temperature indicated that the reactions which destroy hydrogen atoms must have but an insignificant heat of activation. To account for their observations, they suggested that hydrogen atoms react with ammonia to form NH_4 molecules, decomposition of the latter at temperatures above 300°C. shifting the equilibrium to the left. At small ammonia pressures, the establishment of equilibrium was prevented by the diffusion of hydrogen atoms to the wall. Two reactions were accordingly suggested to account for the low quantum yield in the ammonia decomposition, $NH_4 + NH_2 \rightarrow 2NH_3$ and $NH_4 + NH_2 \rightarrow NH_3 + NH + H_2$, the first being three hundred times as probable as the second. The rise of the quantum yield observed to occur at temperatures over 400°C. may be due to the above equilibrium moving so far to the left that not sufficient NH_4 remains to produce ammonia by either of these reactions.

Recently, the range of ammonia pressures over which the quantum yield is independent of the ammonia pressure has been extended to cover pressures of 1.2 to 8.5 atmospheres.[221] The yield is also independent of wave-length. The value found (0.14) was, however, lower than that of other investigators. A rather rapid increase of quantum yield with temperature was found, the values being 0.34 at 250°C. and 0.54 at 400°C., a result intermediate between those of Kuhn and of Wiig and Kistiakowsky. The method suggested for the disappearance of

[216] Mund, W., and van Tiggelen, A., *Bull. Soc. Chim. Belg.*, **46**, 104, 227 (1937); *Ann. Soc. Sci. Bruxelles*, **Ser. I**, 57, 92 (1937); *Chem. Abs.*, **31**, 5685, 6560, 6971 (1937). These authors devise a mechanism which avoids reaction (2). See also Mund, W., Brenard, G., and Kaertkemeyer, L., *Bull. Soc. Chim. Belg.*, **46**, 211 (1937). For a further discussion of these relatively inaccessible papers, see Taylor, H. S., *J. Phys. Chem.*, **42**, 783 (1938).

[217] Boehm, E., and Bonhoeffer, K. F., *Z. physik. Chem.*, **119**, 385 (1926); Taylor, H. S., and Jungers, J. C., *J. Chem. Physics*, **2**, 452 (1934).

[218] Taylor, H. S., and Jungers, J. C., *J. Chem. Physics*, **2**, 452 (1934).

[219] A similar conclusion was reached by Melville, H. W., from work on the mercury-sensitized reaction [*Trans. Faraday Soc.*, **28**, 885 (1932)].

[220] Farkas, L., and Harteck, P., *Z. physik. Chem.*, **25B**, 257 (1934).

[221] Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **56**, 318 (1934).

hydrazine assumed the reactions $H + N_2H_4 \rightarrow NH_3 + NH_2$ and $2NH_2 + N_2H_4 \rightarrow 2NH_3 + N_2 + H_2$. The former was regarded as the more probable.[222] The decomposition of hydrazine was regarded as a photochemical process sensitized by ammonia.

Wiig[223] finds that as the ammonia pressure is increased from zero the quantum yield at 2100A rises from about 0.1 to a maximum of about 0.3 at 65 to 120 mm. pressure and then gradually falls off to about 0.18 at 840 mm. The average value is about that of Warburg, 0.25. The results agree with those of Ogg, Leighton and Bergstrom. It was also observed[224] that the values depend to some extent upon the size of the reaction cell, decreasing in a cell of larger diameter. The reaction appears to become heterogeneous at ammonia pressures less than about 300 mm. and may be partly heterogeneous at higher pressures. Welge and Beckman[225] detected the formation of hydrazine during the early stages of the reaction. The non-condensible portions of the gases had higher proportions of hydrogen than 75 per cent. At this early stage of decomposition, effected by the 1990A line, the quantum yields averaged 0.87 and appeared to approach unity as a limit. The high quantum yields made it seem that recombination of the primarily formed NH_2 and H is not as important as had formerly appeared to be the case. A small amount of hydrazine may, however, be decomposed by hydrogen atoms with the formation of ammonia and nitrogen. The effect of the latter reaction becomes more exaggerated as the reaction proceeds.

During the early period of the investigation of the reaction of ammonia on irradiation considerable light was thrown upon it by studies on the mercury-sensitized reaction.[226] It was, for example, in the case of the mercury-sensitized reaction that Taylor and Bates[227] observed the reaction products to contain 89 per cent of hydrogen and 11 per cent of nitrogen, a circumstance which led to the development of mechanisms permitting the formation of hydrazine. Dickinson and Mitchell,[228] who obtained 70 mole per cent of hydrogen, found the presence of argon and nitrogen at 0.3 mm. pressure had little effect on the reaction rate. On the other hand, hydrogen at 0.3 mm. and lower pressures had a large inhibiting effect, which increased with increasing ammonia pressures. Melville[229] observed that in the presence of mercury vapor and hydrogen, the decomposition was less rapid when the ammonia was irradiated simultaneously by a mercury arc and a zinc spark than when irradiated by the zinc spark alone. The mercury resonance line dissociates the hydrogen. The resulting hydrogen atoms were believed to recombine with the NH_2 groups (formed by the predissociation of the ammonia by the zinc lines) more rapidly owing to the higher partial pressure of hydrogen atoms under these conditions. Gedye and Rideal[230] found but little hydrazine produced in the mercury-sensitized reaction. The following mechanism is proposed by Welge and Beckman.[231]

[222] See Dixon, J. K., *J. Am. Chem. Soc.*, **54**, 4262 (1932), and Wenner, R. R., and Beckman, A. O., *Ibid.*, **54**, 2787 (1932).

[223] Wiig, E. O., *J. Am. Chem. Soc.*, **57**, 1559 (1935).

[224] Wiig, E. O., *J. Am. Chem. Soc.*, **59**, 827 (1937).

[225] Welge, H. J., and Beckman, A. O., *J. Am. Chem. Soc.*, **58**, 2462 (1936).

[226] Dickinson, R. G., and Mitchell, A. G., *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

[227] Taylor, H. S., and Bates, J. R., *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).

[228] Dickinson, R. G., and Mitchell, A. C. G., *J. Am. Chem. Soc.*, **49**, 1478 (1927).

[229] Melville, H. W., *Trans. Faraday Soc.*, **28**, 885 (1932).

[230] Gedye, G. R., and Rideal, E. K., *J. Chem. Soc.*, 1160 (1932).

[231] Welge, H. J., and Beckman, A. O., *J. Am. Chem. Soc.*, **58**, 2462 (1936).

$$Hg + h\nu \longrightarrow Hg'$$
$$Hg' + NH_3 \longrightarrow NH_3' + Hg$$
$$NH_3' \longrightarrow NH_3 + h\nu_2$$
$$NH_3' \longrightarrow NH_2 + H$$

The low quantum yield of 0.12 was attributed to the occurrence of the fluorescence reaction.

Rate expressions were derived for this and the corresponding deuteroammonia (ND_3) reaction by Evans and Taylor.[232] Melville[233] suggests that the decompositions are brought about in collisions between ammonia or ND_3 and metastable atoms. The metastable atoms are produced from quenching collisions between $^3P_1$ atoms and ammonia or ND_3, the latter two being equally efficient. To account for the observed greater reactivity of ammonia, secondary reactions, unconnected with the mercury atom processes, were assumed. The quantum yield for the photosensitized reaction is about the same as that of the direct decomposition, so that the secondary reactions are the same.[234]

Berthelot and Gaudechon[235] exposed mixtures of ammonia and oxygen to the total radiation of the mercury arc and found nitrogen, hydrogen and water, but no nitrates or nitrites, as products of the reaction. The reaction produced by the 2080A line of the zinc spark was more complex, according to Bacon and Duncan,[236] since ammonium nitrate and smaller amounts of ammonium nitrite could be obtained. The process $NH_2 + O_2 \rightarrow NO + H_2O$ was assumed and the overall reaction could be written: $8NH_3 + 7O_2 \rightarrow 2N_2 + 2NH_4NO_3 + 8H_2O$.

The photochemical reaction of ammonia with carbon monoxide yields formamide as a primary product. The amide then undergoes secondary reactions.[237] Less than 5 per cent of the reacting ammonia yields hydrogen and nitrogen. The rate of ammonia decomposition approximately doubles in the presence of carbon monoxide. Methylamine and ethylamine also react with carbon monoxide, a much larger amount of gaseous decomposition products being formed than in the reaction of ammonia.

The Photochemical Decomposition of Hydrazine. Faint diffuse absorption bands (apparently predissociation bands) begin at about 2490A in 80 cm. layers of hydrazine vapor at 0.5 mm. pressure.[238] Continuous absorption begins at about 2370A (at 2260A in 20 cm. layers). Hilgendorff[239] gives the heat of dissociation as 122.4 kcal. per mole.

Elgin and Taylor found that radiations shorter than 2400A decompose hydrazine by the reaction: $2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2$, the ammonia subsequently decomposing at a rate about one-tenth that of the hydrazine decomposition rate. The hydrazine decomposition rate is independent of temperature, and of the addition of nitrogen, hydrogen or ammonia. The reaction can also be sensitized to the 2537A mercury line by the addition of mercury vapor; in this case the rate of the hydrazine decomposition so greatly exceeds that of the ammonia (40 times) that

[232] Evans, M. G., and Taylor, H. S., *J. Chem. Physics*, **2**, 732 (1934).
[233] Melville, H. W., *Proc. Roy. Soc.*, **152A**, 325 (1935).
[234] Farkas, L., and Melville, H. W., *Proc. Roy. Soc.*, **157A**, 621, 625 (1936); for the direct unsensitized decomposition of deuteroammonia, see Wiig, E. O., *J. Am. Chem. Soc.*, **59**, 955 (1937).
[235] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1327 (1910); see also Rakestraw, N. W., and Hollaender, A., *Science*, **84**, 442 (1936).
[236] Bacon, H. E., and Duncan, A. B. F., *J. Am. Chem. Soc.*, **56**, 336 (1934).
[237] Emeléus, H. J., *Trans. Faraday Soc.*, **28**, 89 (1932).
[238] Elgin, J. C., and Taylor, H. S., *J. Am. Chem. Soc.*, **51**, 2059 (1929); see also Imanishi, M., *Nature*, **127**, 782 (1931).
[239] Hilgendorff, H. J., *Z. Physik*, **95**, 781 (1935).

a nearly complete separation of the two reactions is possible. Indeed, it is the most rapid reaction obtained by means of excited mercury. The rate of the sensitized reaction is 110-120 times the rate of the direct photochemical decomposition. It is a chain reaction, the quantum yield being about 13. The rate of the sensitized reaction also is unaffected by nitrogen, ammonia or hydrogen added separately, although apparently the addition of both hydrogen and ammonia retards the reaction rate. The lack of retardation by hydrogen alone is explained by the assumption that hydrogen atoms react with hydrazine. The rate of the sensitized reaction is directly proportional to the incident light intensity.

The observed facts regarding the direct photochemical reaction could be explained by the assumption of a primary process leading either to a dissociation into N_2H_3 and H or into two NH_2 radicals.

The quantum yields produced by monochromatic light of 1990A, were found by Wenner and Beckman[240] to range from 1.0 at a pressure of 2 mm. to 1.7 at 14 mm. The composition of the gases produced in the initial stages of the reaction was not in agreement with those reported by Elgin and Taylor. More hydrogen formed at the low hydrazine pressures than at the higher ones. The mechanism must differ from that of the mercury-sensitized reaction, because of the excess of hydrogen formed and because of the much lower quantum yield. Their suggested mechanism involved the reactions

$$N_2H_4 + h\nu \longrightarrow N_2H_3 + H$$
$$H + N_2H_4 \longrightarrow N_2H_3 + H_2$$
$$2N_2H_3 \longrightarrow 2NH_3 + N_2$$
$$2N_2H_3 \longrightarrow N_2 + H_2 + N_2H_4 \text{ (wall reaction)}.$$

The Decomposition of Hydrogen Azide. The ultraviolet irradiation of aqueous solutions of hydrogen azide yields mainly hydroxylamine and nitrogen with small amounts of ammonia and traces of hydrazine.[241] Gaseous hydrogen azide, on brief illumination with the 1990A line, gives a gas, non-condensable at liquid air temperatures; on longer illumination, a white solid, presumably ammonium azide, NH_4N_3, is formed.[242] Light absorption by gaseous hydrogen azide sets in at 2200A. The decomposition proceeds by two concurrent reactions, one yielding hydrogen and nitrogen, and the other ammonia and nitrogen.

$$2HN_3 \longrightarrow H_2 + 3N_2 \text{ and } 3HN_3 \longrightarrow NH_3 + 4N_2$$

Over a pressure range of two to 130 mm., three molecules are decomposed per absorbed quantum, when calculated to the formation of ammonia. When sensitized by mercury vapor, there are also two concurrent reactions during the early part of the run, although their relative extents differ from those observed in the unsensitized reaction.

During the early period of the photosensitized reaction, the ammonia formed reacts with excess hydrogen azide to form solid ammonium azide. When the pressure has reached a value 1.18 times its initial value, excess hydrogen azide has all been consumed. After this, ammonia formed by the decomposition of ammonium azide remains as a gas and results in a sudden increase in the rate of change of total pressure. As the decomposition nears completion, a new reaction

[240] Wenner, R. R., and Beckman, A. O., *J. Am. Chem. Soc.*, **54**, 2787 (1932).
[241] Gleu, K., *Ber.*, **61**, 702 (1928).
[242] Beckman, A. O., and Dickinson, R. G., *J. Am. Chem. Soc.*, **50**, 1870 (1928); **52**, 124 (1930); Myers, A. E., and Beckman, A. O., *Ibid.*, **57**, 89 (1935).

$H_2 + HN_3 \rightarrow NH_3 + N_2$ becomes increasingly important. When the pressure becomes constant no hydrogen remains, and the end products are given by $3HN_3 \rightarrow NH_3 + 4N_2$.

The quantum yield of the photosensitized reaction in its initial stage is 3.6; at pressures below 2 mm. the yield decreases rapidly. The value is in agreement with a calculated value of 3.4 molecules of HN_3 decomposed by either reaction per quantum absorbed, calculated to the formation of ammonium azide. The following possible partial reactions may be written:

$$(1)\quad Hg + h\nu \longrightarrow Hg^*$$
$$(2)\quad Hg^* + HN_3 \longrightarrow Hg + N_2 + HN$$
$$(3)\quad HN + HN_3 \longrightarrow H_2 + 2N_2$$
$$(4)\quad HN + HN_3 \longrightarrow N_2 + N_2H_2$$
$$(5)\quad N_2H_2 + HN_3 \longrightarrow 2N_2 + NH_3$$
$$(6)\quad NH_3HN_3 \longrightarrow NH_4N_3 \text{ (solid)}.$$

18 per cent of the molecules react by (2) and (3) and 82 per cent by (2), (4), (5) and (6).

Reactions Involving the Oxides of Nitrogen. A direct combination of nitrogen and oxygen under the influence of rays from a quartz mercury arc occurs to a very slight extent.[243] Kondrat'ev [244] states that the amount of combination can be doubled by the addition of 5 per cent of hydrogen or of 28 per cent of carbon monoxide. The addition of both gases increases the yield ten times. It is assumed that excited oxygen molecules are involved in the combination process.

Nitrous Oxide. In the absorption spectrum of this gas there have been observed bands of nitric oxide. The presence of the latter is probably due to a photochemical decomposition occurring during the measurements.[245] Sen-Gupta [246] found that nitrous oxide absorbs light at 1850A, transmits better at about 1700A and absorbs again at 1580A. It was suggested that these absorptions represent dissociations into NO and nitrogen atoms in different metastable states. That produced by 1850A was said to be ^2D and that at 1580A ^2P. In each region the absorption is continuous.[247] Absorption begins at longer wave-lengths as the temperature is increased (2246A at 20°C. and 2604 at 675°C.). By plotting the wave-length of beginning absorption against temperature and extrapolating to 0°, (2140A) it was deduced that the minimum energy required for the dissociation into NO and N is 132 kcal. From studies on mixtures of nitrogen peroxide with nitrous oxide, Henriques, Duncan and Noyes [248] concluded that in the direct decomposition of the latter, a second primary process $N_2O + h\nu \rightarrow N_2 + O$ is also necessary to explain the observed quantum yields.

Macdonald [249] irradiated nitrous oxide at various pressures with radiations

[243] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1517 (1910). They found also that nitrous and nitric oxides are each decomposed into their elements, some of each gas reacting with liberated oxygen to form higher oxides.

[244] Kondrat'ev, V., *Acta Physicochim. U.R.S.S.*, **3**, 247 (1935); *Chem. Abs.*, **30**, 6649 (1936).

[245] Lambrey, M., *Compt. rend.*, **186**, 1112 (1928).

[246] Sen-Gupta, P. K., *Proc. Roy. Soc.*, **146A**, 824 (1934); *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **3**, 197 (1934); *Chem. Abs.*, **29**, 7806 (1935).

[247] Henry, L. A., *Compt. rend.*, **200**, 656 (1935); *J. chim. phys.*, **32**, 437 (1935). See also Dutta, A. K., *Proc. Roy. Soc.*, **138A**, 84 (1932).

[248] Henriques, F. C., Jr., Duncan, A. B. F., and Noyes, W. A., Jr., *J. Chem. Physics*, **6**, 518 (1938).

[249] Macdonald, J. Y., *J. Chem. Soc.*, **1 (1928)**; *cf.* also Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **59**, 807 (1937).

(1860-1990A) from a condensed aluminum spark. The decomposition proceeded in accordance with the equation:

$$4N_2O \longrightarrow 2NO + O_2 + 3N_2.$$

The quantum efficiency was 3.9 and was fairly independent of the pressure (21 to 607 mm.) and temperature (0° to 40°).

Excited mercury atoms can bring about the decomposition.[250] In this case, nitrogen is liberated and the oxygen combines with the mercury, nitric oxide not being produced. The reaction velocity is proportional to the intensity of the 2537A line employed to excite the mercury.

A mercury-sensitized chain reaction between nitrous oxide and hydrogen has been studied by Melville.[251] Oxygen participates in both the making and breaking of the chains, the length of chains being approximately the same for the photochemical and the thermal reactions.

Nitric Oxide. Leifson [252] found an intense banded absorption to begin at 2264A. There are at least four groups of bands, which are interpreted as arising from combinations of four electronic levels with the ground state of the molecules.[253] No regions of continuous absorption are apparent.

Macdonald [254] found the decomposition produced by irradiating the gas with radiations of wave-lengths 1860-1990A to follow two courses. Ninety per cent of the decomposition yielded nitrogen and oxygen and 10 per cent followed the equation $3NO \rightarrow N_2O + NO_2$. The quantum efficiency in this case is given as 0.73. The data were interpreted in terms of a theory of excited molecules serving as intermediaries, since the spectral data did not indicate the nature of the bands to be suggestive of predissociation.

On the other hand, Flory and Johnston [255] have interpreted the primary process as one of predissociation, at least when the pressure was low (0.02 to 7 mm.). The final products of the reaction were found to be nitrogen and oxygen, the latter being partly destroyed by a reaction occurring when the gas was compressed in a McLeod gauge. In this process, a solid product presumably mercurous nitrate, was formed. It was shown that mercury [256] vapor in the apparatus from the gauge did not essentially affect the results and that the reaction was at least 98 per cent non-sensitized since the use of a mercury vapor filter failed to reduce the rate of decomposition. The use of a Blue-Purple Corex A filter which cuts off the radiation completely below 2300A, but shows 70 per cent transmission of the 2537A line, reduced the rate to 1.3 per cent of its value without the filter. A similar experiment with a Cellophane filter cutting out radiation below 2200A and transmitting 45 per cent of that of the 2537A line reduced the rate to about 1 per cent of that without the filter.[257]

The rate of decomposition was directly proportional to the rate of absorption

[250] Manning, W. M., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **54**, 3907 (1932).

[251] Melville, H. W., *Proc. Roy. Soc.*, **146A**, 737 (1934).

[252] Leifson, S. W., *Astrophys. J.*, **63**, 73 (1926).

[253] Sponer, H., and Hopfield, J. J., *Phys. Rev.*, **27**, 640 (1926); Jenkins, F. A., Barton, H. A., and Mulliken, R. S., *Phys. Rev.*, **30**, 150, 175 (1927); Lambrey, M., *Compt. rend.*, **186**, 1112 (1928); **187**, 210 (1928); **189**, 574 (1929); **190**, 261 (1930).

[254] Macdonald, J. Y., *J. Chem. Soc.*, 1 **(1928)**.

[255] Flory, P., and Johnston, H., *J. Am. Chem. Soc.*, **57**, 2641 (1935).

[256] *Cf.* also Kondrat'ev, V., *Acta Physicochim. U.R.S.S.*, **3**, 247 (1935); *Chem. Abs.*, **30**, 6649 (1936).

[257] Under other conditions, however, Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **53**, 514 (1931) found good evidence for the existence of a mercury-sensitized reaction. Under his conditions, there was no direct reaction. The differences in the manner of operation of the mercury arc source were, however, such that the results of these observers may not have been contradictory.

of the effective wave-lengths. At very low pressures, the rate was also directly proportional to the pressure, a circumstance which eliminated an excited molecule mechanism. Were the primary process of the latter type, the rate would vary as the square of the pressure since collisions with normal molecules would be required to effect a decomposition of the excited molecules. Most of the reaction produced by the mercury arc was attributed to absorption of the 1832A line by the *delta* band of nitric oxide. Absorption of the 1849A line in the *beta* band may have a lesser effect which becomes significant at higher pressures in agreement with the rates observed at pressures above 3 mm. Sparks between aluminum, zinc, cadmium, nickel, copper and tin electrodes were effective to the same order of magnitude. The activity of such sparks was regarded as due primarily to absorption in the continuous background. That the process is one of predissociation finds some support in the work of Kaplan[258] on the emission bands of the gas. A calculated value for the molal heat of dissociation of nitric oxide, 121.95 kcal., is less than the energy of the 1830A line by 33.6 kcal. The dissociation products must, however, be normal atoms. The only secondary processes in the reaction are recombination processes occurring at the walls. It is suggested that at higher pressures the primary step may be predissociation from the upper levels of the *beta*-bands, rather than from the *delta*-bands.

Nitrogen Peroxide. At room temperatures this gas is composed of an equilibrium mixture of NO_2 and N_2O_4 molecules. The latter is non-absorbing in the visible range and the former is colored. Harris[259] found the single molecules to exhibit a banded absorption spectrum between 6000 and 2250A. Lambrey[260] tabulated the wave-lengths of the apparent absorption maxima and the individual intensities of the lines for the region 2083 to 4009A. The NO_2 molecule exhibits two limits of predissociation.[261] The first lies between 3800 and 3700A and the second between 2459 and 2200A. The diffuse bands of the first region extend to about 2596A, at which point they are suddenly replaced by a series of sharply defined bands probably coinciding with a different electronic transition. These bands then become diffuse at the second predissociation limit. The first limit corresponds to a dissociation into NO and a normal oxygen atom, the second to the production of an oxygen atom in the ^1D state.[262] The absorption attributed to the N_2O_4 molecules also present in the gas is continuous,[263] consisting of two broad structureless bands at about 3400 and 2400A.[264]

On irradiation by means of the mercury arc, nitrogen peroxide was found by Norrish[265] to exhibit a marked pressure increase. Since radiations transmitted by glass caused the pressure increase, the latter was attributed to a photochemical decomposition of the NO_2 molecules into nitric oxide and oxygen. The addition of either of these products completely reversed the reaction, nitric oxide being the more effective in displacing the equilibrium. The pressure increases rapidly at first, then slows down. The increase is complete in about fifteen minutes; when the illumination is stopped the pressure returns to its original value, rapidly at

[258] Kaplan, J., *Phys. Rev.*, **37**, 1406 (1931).
[259] Harris, L., *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).
[260] Lambrey, M., *Compt. rend.*, **188**, 251 (1929); see also Lambrey, M., and Corbière, J., *Compt. rend.*, **201**, 1334 (1935).
[261] Henri, V., *Nature*, **125**, 202 (1930).
[262] Mecke, R., *Z. physik. Chem.*, **7**, 127 (1930); Herzberg, G., *Z. physik. Chem.*, **10**, 189 (1930); Ionescu, A., *J. phys. radium*, **8**, 369 (1937).
[263] See also Carwile, L., *Astrophys. J.*, **67**, 184 (1928).
[264] *Cf.* Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 630 (1934).
[265] Norrish, R. W. G., *J. Chem. Soc.*, 761 (1927).

first and then more slowly. Constancy of pressure was attained when the rate of recombination of NO and oxygen became equal to the rate of the photodecomposition. Hydrogen had no effect on the increase of pressure. This work had been completed before the interpretation of the spectrum by Henri had appeared. Norrish, lacking this information, proposed a mechanism involving a reaction between an excited and a normal molecule of NO_2 in which molecular oxygen was produced.

By a method insuring only very low partial pressures of the reaction products, Dickinson and Baxter[266] were able to avoid the recombination of the products and the resulting heat effect. Under their conditions, it was not necessary to treat the reaction as an equilibrium and quantum yields could be determined for the direct decomposition. The yields were determined in a series of spectral regions, isolated by the use of filters. The following mean values, expressed as molecules of oxygen per quantum absorbed, were obtained: 4350A, 0.0046; 4050A, 0.036; 3660A, 0.77. At the low pressures used, the values were not markedly dependent on the pressure.

These observations were extended by Norrish[267] to include six wave-lengths. The yield was zero at 5760, 5460 and 4360A. For 4050A, it was 0.37, at 3650A 1.05 and for the range 3160 to 2650A, 1.04. It is particularly interesting that a photochemical threshold is found in the middle of a region in which the substrate absorbs strongly, the maximum absorption of nitrogen peroxide being at about 4500A where the quantum yield is zero. Light of the photochemically inactive wave-length 4360A produced an orange fluorescence and the violet light of 4050A, which is only partly effective photochemically, a much fainter greenish-yellow fluorescence. The spectra of the fluorescence at each wave-length possessed two wide maxima at about 6400 and 5900A, different intensity distributions accounting for the difference in color. At 3650A only a very faint fluorescence could be produced. When present, the fluorescence could be destroyed by the addition of oxygen. These observations can now be interpreted as evidence that predissociation begins at about the threshold region, necessitating a revision of previously assumed excited molecule mechanisms.

The presence of nitrogen pentoxide does not affect the decomposition of the nitrogen peroxide, according to Holmes and Daniels.[268] Their quantum yields, based on molecules of NO_2 decomposed, in a mixture of the above gases were 1.92 at 3130A, 1.83 at 3660A, 0.5 at 4050A and zero at 4360A. They also found that N_2O_4 is decomposed at 2650A with a quantum efficiency of 0.6. Although the lines 3660 and 3130A are absorbed by this gas, no measurable decomposition results. Helium, argon, nitrogen, oxygen, hydrogen, carbon dioxide and nitrous oxide were found to decrease the photolysis of NO_2, but were more effective in reducing fluorescence.

The synthesis of nitrogen dioxide in a glow discharge in a two to one oxygen : nitrogen mixture has been reported by Westhaver and Brewer.[269]

Nitrogen Pentoxide. The absorption of this gas, according to Urey, Dawsey and Rice[270] is continuous from 3050A into the Schumann region. The upper

[266] Dickinson, R. G., and Baxter, W. P., *J. Am. Chem. Soc.*, **50**, 774 (1928).
[267] Norrish, R. W. G., *J. Chem. Soc.*, 1158, 1604, 1611 (1929).
[268] Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 630 (1934).
[269] Westhaver, J. W., and Brewer, A. K., *J. Phys. Chem.*, **34**, 554 (1930).
[270] Urey, H. C., Dawsey, L. H., and Rice, F. O., *J. Am. Chem. Soc.*, **51**, 3190 (1929). See also Jones, E. J., and Wulf, O. R., *J. Chem. Phys.*, **5**, 873 (1938).

absorption limit corresponds with an energy of 93.2 kcal, suggesting that the primary reaction $N_2O_5 \rightarrow 2NO_2 + O$ occurs.

Holmes and Daniels,[271] who also gave absorption data, stated that light of wave-lengths 2800 and 2650A decomposes the pentoxide with a quantum efficiency of 0.6.

Nitrogen pentoxide is also decomposed photochemically by blue light, but only in the presence of nitrogen peroxide as a sensitizer.[272] Light in the region 4000 to 4600A is responsible for the reaction, the rate being proportional to the energy absorbed by the nitrogen peroxide. At low concentrations of the sensitizer, the rate is proportional to the amount present. From the data given, Kistiakowsky [273] has calculated an upper quantum yield limit of about 18.

Fazel and Karrer [274] suggested that the excited nitrogen peroxide molecules transferred their energy by collisions of the second kind to molecules of nitrogen pentoxide, thereby dissociating the latter. Norrish,[275] however, suggested that the nitrogen peroxide might be decomposed, the resulting nitric oxide molecules then reacting with nitrogen pentoxide with the production of three molecules of nitrogen peroxide, the original sensitizer. Busse and Daniels [276] found the rate of this photosensitized reaction to be unaffected by collisions with oxygen, nitrogen or hydrogen. Bromine could not be substituted for the nitrogen peroxide even though the halogen has a rather similar absorption range. When added to a mixture containing nitrogen peroxide, bromine decreases the sensitizing efficiency of the latter, probably by absorbing a portion of the effective light. From measurements of the relative rates of decomposition of nitrogen pentoxide at 0°C. by radiations of wave-lengths 4350, 4050 and 3660A, and comparison with the data on the decomposition of nitrogen dioxide, Baxter and Dickinson [277] concluded the mechanism of the sensitized nitrogen pentoxide decomposition to be essentially that suggested by Norrish.

Nitrosyl Chloride. Magnanini [278] found nitrosyl chloride to exhibit weak absorption bands in the region 5300-6200A; strong absorption sets in at 5300A. Kistiakowsky [279] states that the absorption begins above 6300A and increases gradually toward the ultraviolet. In the region between 5100 and 4350A the banded structure showed faint but diffuse line structure. In the ultraviolet below the absorption maximum at 3300A no banded structure could be observed at all.

According to Kiss [280] visible light decomposes nitrosyl chloride incompletely into nitric oxide and chlorine, which recombine in the dark, a stationary state being finally reached. The temperature coefficient is unity (0° to 78°C.). Working with the spectral regions 4380-5000 and 4480-5200A, isolated by means of filters, Bowen and Sharp [281] found the quantum yield to be 0.5 independent of the extent of the decomposition. Their proposed mechanism included a primary dissociation into nitric oxide and a chlorine atom, followed by some secondary reactions in which the chlorine atom produced the transitory compound $NOCl_2$. Quite different

[271] Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 630 (1934).
[272] Daniels, F., and Johnston, E. H., *J. Am. Chem. Soc.*, **43**, 72 (1921).
[273] Kistiakowsky, G. B., "Photochemical Processes," The Chemical Catalog Co., Inc., (Reinhold Publishing Corp.), New York, **1928**, 140.
[274] Fazel, C. S., and Karrer, S., *J. Am. Chem. Soc.*, **48**, 2837 (1926).
[275] Norrish, R. W. G., *Nature*, **119**, 123 (1927).
[276] Busse, W. F., and Daniels, F., *J. Am. Chem. Soc.*, **49**, 1257 (1927).
[277] Baxter, W. P., and Dickinson, R. G., *J. Am. Chem. Soc.*, **51**, 109 (1929).
[278] Magnanini, G., *Z. physik. Chem.*, **4**, 427 (1889).
[279] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **52**, 102 (1930).
[280] Kiss, A., *Rec. trav. chim.*, **42**, 665 (1923).
[281] Bowen, E. J., and Sharp, J. F., *J. Chem. Soc.*, **127**, 1026 (1925).

results were reported by Kistiakowsky,[282] who obtained a quantum yield of 2.1 at each of several wave-lengths from 6350 to 4350A, and probably also at 3650A. No explanation could be given for the divergence from the results of Bowen and Sharp. Kistiakowsky also believed the spectral evidence favored an interpretation by means of excited nitrosyl chloride molecules rather than one of direct dissociation for the primary process.

Nitrogen Trichloride. The decomposition of nitrogen trichloride

$$2NCl_3 \longrightarrow N_2 + 3Cl_2$$

is sensitized by chlorine, the velocity being directly proportional to the light absorbed by the added chlorine.[283]

The reaction is of zero order with respect to nitrogen trichloride until the decomposition is practically complete; a semi-explosive reaction then occurs. With pressures of nitrogen trichloride of 0.146 to 2.48 mm. and of chlorine between 100 and 22 mm. the quantum efficiencies (at 4360 and 3650A) were high, between 17 and 5, depending on the pressure of the chlorine. They tended to approach a limiting value of about three at the highest pressures of chlorine. If the vessel is treated with water or heated to 100°C., the efficiency is abnormally high; the "maturing" of a vessel is chiefly the formation of an invisible film of ammonium chloride on the surface which indirectly establishes a constant condition of chain rupture in the gas phase. The relation between the yield and the chlorine pressure is given by

$$\frac{1}{0.0038P_{Cl_2}} = K_1$$

in which K_1 varies from 2.0 to 2.5 and is dependent on the size of the vessel. Foreign gases reduce the quantum yield to a limiting value of two, the relation being

$$\frac{1}{(0.0038P_{Cl_2} + K_2P_{Gas})} = 2.5.$$

The K_2 values were: helium 0.00093, argon 0.0016, nitrogen 0.0017, oxygen 0.0025 and carbon dioxide 0.0038. It was suggested that the added gas stabilizes by triple collisions an energy-rich complex, NCl_4, which is associated with the rupture of chains.

The Photochemistry of Sulfur Compounds

The gaseous reaction between hydrogen and sulfur is greatly aided by the ultraviolet rays from a mercury vapor lamp, according to Norrish and Rideal.[284] The absorption spectrum of sulfur vapor contains a band with maximum absorption at 2750A according to Graham.[285] It is known that this value lies within one of the two predissociation regions possessed by sulfur vapor.[286]

The absorption of hydrogen sulfide, which is entirely continuous, begins at about 2800A and reaches a maximum at about 1850A.[287] The gas can be decom-

[282] Kistiakowsky, G. B., *loc. cit.*
[283] Griffiths, J. G. A., and Norrish, R. W. G., *Proc. Roy. Soc.*, **130A**, 591 (1931); **135A**, 69 (1932).
[284] Norrish, R. W. G., and Rideal, E. K., *J. Chem. Soc.*, **125**, 2070 (1924); **123**, 3202 (1923).
[285] Graham, J. I., *J. Chem. Soc.*, **98** (ii), 1015 (1910).
[286] Christy, A., and Naudé, S. M., *Phys. Rev.*, **37**, 903 (1931).
[287] Goodeve, C. F., and Stein, N. O., *Trans. Faraday Soc.*, **27**, 395 (1931).

posed by the light of the mercury arc [288] or of the zinc spark. Using the latter source, Stein [289] found the quantum yield to be 2 (2050A) when the hydrogen sulfide pressure was 250 mm. At higher pressures the quantum yield reached 3.8. The nature of the primary process was not determined. On the other hand, Forbes, Cline and Bradshaw [290] find the yield to be unity and independent of pressure between 8 and 1400 mm. and of light flux over a 14-fold range at 2080A.

The Oxides of Sulfur. Sulfur monoxide, spectral evidence for the existence of which has been presented by Henri and Wolff,[291] is said to undergo a photochemical decomposition when irradiated by the shorter ultraviolet wave-lengths.[292] A slight contraction in volume of sulfur dioxide was observed by Berthelot and Gaudechon [293] to occur in a sample of the gas irradiated over a mercury surface. Sulfur was deposited on the tube and the mercury became encrusted with a sulfate. Corresponding results were also obtained in the presence of oxygen. Similar observations have been reported by Hill,[294] who used a Uviol mercury lamp. He represented the decomposition as $3SO_2 \rightarrow 2SO_3 + S$. By interposing various filters it was found that the chief response is at 3130A, lying within the first absorption band of sulfur dioxide. The gas has a well-developed band system which extends from about 3400A to shorter wave-lengths.[295] Predissociation into SO and O sets in at about 1950-1900A. Predissociation also is possible at about 2100A.[296]

Kornfeld and McCaig [297] obtained the absorption spectrum of sulfur dioxide before and after it had been irradiated at low temperatures with an aluminum spark.

Although the gas decomposes at these wave-lengths into SO and O, the spectrum of SO was not observed. Because of its surplus vibrational energy, the latter was possibly consumed in an unexpectedly rapid reaction.

The spectrum of sulfur trioxide shows continuous absorption from 3300 to 2600A and from 2300 to 2000A.[298] Kornfeld [299] concludes that at 2760A dissociation produces SO_2 and a normal state oxygen atom.

Konstantinova-Shlezinger [300] states that the sulfur trioxide produced when sulfur dioxide is irradiated in a quartz vessel, is decomposed to some extent by the reaction $2SO_3 \rightarrow 2SO_2 + O_2$.

The Oxidation of Sulfur Dioxide. Coehn and Becker [301] found that the formation of sulfur trioxide proceeds fairly rapidly in a mixture of sulfur dioxide and oxygen in a quartz reaction vessel mounted within a mercury lamp. With a mixture of equal volumes of sulfur dioxide and oxygen, the content of sulfur trioxide was 65 per cent at equilibrium. The latter condition was attained within an hour at a temperature of 160°C. This is quite different from the thermal equilibrium, since in daylight at temperatures below 450°C., there is practically 100 per

[288] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1517 (1910).
[289] Stein, N. O., *Trans. Faraday Soc.*, **29**, 583 (1933).
[290] Forbes, G. S., Cline, J. E., and Bradshaw, B. C., *J. Am. Chem. Soc.*, **60**, 1431 (1938).
[291] Henri, V., and Wolff, F., *J. Phys. Radium*, **10**, 81 (1929).
[292] Cordes, H., and Schenk, P. W., *Trans. Faraday Soc.*, **30**, 31 (1934).
[293] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1517 (1910).
[294] Hill, R. A., *Trans. Faraday Soc.*, **20**, 107 (1924); see also Konstantinova-Shlezinger, M., *J. Phys. Chem. (U.S.S.R.)*, **6**, 601 (1935); *Chem. Abs.*, **29**, 7809 (1935).
[295] Watson, W. W., and Parker, A. E., *Phys. Rev.*, **37**, 1484 (1931); Henri, V., and Wolff, F., *J. Phys. Radium*, **10**, 81 (1929); Chow, T.-C., *Phys. Rev.*, **44**, 638 (1933); Wieland, K., *Nature*, **130**, 847 (1932); *Trans. Faraday Soc.*, **30**, 260 (1934).
[296] Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932).
[297] Kornfeld, G., and McCaig, F., *Trans. Faraday Soc.*, **30**, 991 (1934); *Chem. Abs.*, **29**, 680 (1935).
[298] Dutta, A. H., *Proc. Roy. Soc.*, **137A**, 366 (1932).
[299] Kornfeld, G., *Trans. Faraday Soc.*, **33**, 614 (1937).

cent sulfur trioxide at equilibrium. The irradiation equilibrium was found not to be displaced by increases of temperature up to 800°C., whereas the dark equilibrium is displaced considerably when the temperature is raised above 450°C. The temperature coefficient of the oxidation rate was found to be 1.2. These authors also made experiments with flowing systems at temperature of 450°C. and obtained yields so high as to lead them to believe a technical process for the production of sulfuric acid to be feasible.[302]

In a repetition of this work, Trautz and Helfrich [303] found the mass law to hold within the limit of experimental error, and observed the equilibrium constant to vary linearly with the square of the current to the mercury arc. The introduction of argon or nitrogen had no effect on the equilibrium constant. They also claimed that completely dried sulfur dioxide neither decomposed when irradiated nor was oxidized in the presence of oxygen.

The quantum yields have been determined for a series of wave-lengths of monochromatic light by Kornfeld and Weegmann.[304] At 2537A and longer wave-lengths, the yield was less than 0.01, and even this was decreased by increasing the concentration of sulfur trioxide. The yields were 0.53 at 2200A, 0.71 at 2070A and 1.0 at 1806A. They attributed the results to a mechanism involving dissociation. The slight yields at the longer wave-lengths were said to be explained by a different mechanism since there is insufficient energy for dissociation. Franck, Sponer and Teller [305] considered the process of oxidation to involve excited molecules of sulfur dioxide. Beyond 1950A, in the predissociation region, they found the quantum yield to rise to three.

Sulfuryl Chloride. The absorption by this material is continuous at wave-lengths less than 2600A.[306] LeBlanc, Andrich and Kangro [307] stated the absorption to begin at 3000A and to rise rapidly at shorter wave-lengths. With radiations absorbed by sulfuryl chloride, but not to a marked extent by either sulfur dioxide or chlorine, there is practically complete dissociation either at 55°C. or at 100°C. These authors believed that irradiation of mixtures of sulfur dioxide and chlorine by wave-lengths absorbed by the former caused only slight changes which did not result in the formation of sulfuryl chloride. On the other hand, radiations absorbed by the chlorine caused the reaction to run to an equilibrium, the position of which depended on the temperature and the amount of moisture present.

Trautz [308] found that the radiations about 2900A caused the combination of the two gases to proceed smoothly as a second order reaction, particularly at higher temperatures. Sulfuryl chloride was not the only product of the reaction; if relatively short periods of exposure were separated by several hours of darkness, other substances formed and decreased the velocity constant. When continuous irradiation was employed, constants were no longer obtained, probably on account of the side reactions. A temperature increase of 80°C. decreased the velocity of the

[300] Konstantinova-Shlezinger, M., *J. Phys. Chem. (U.S.S.R.)*, **6**, 601 (1935); *Chem. Abs.*, **29**, 7809 (1935).
[301] Coehn, A., and Becker, H., *Z. physik. Chem.*, **70**, 88 (1910).
[302] Coehn, A., and Becker, H., German P. 217,772, July 9, 1907.
[303] Trautz, M., and Helfrich, F., *Z. wiss. Phot.*, **33**, 72, 111, 117 (1934); *Brit. Chem. Abs.* **A**, 975, 1183 (1934).
[304] Kornfeld, G., and Weegmann, E., *Z. Elektrochem.*, **36**, 789 (1930).
[305] Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932).
[306] Asundi, R. K., and Samuel, R., *Current Sci.*, **3**, 417 (1935); *Chem. Abs.*, **29**, 3914 (1935).
[307] LeBlanc, M., Andrich, K., and Kangro, W., *Z. Elektrochem.*, **25**, 229 (1919); *Chem. Abs.*, **14**, 493 (1920).
[308] Trautz, M., *Z. Elektrochem.*, **21**, 329 (1915).

combination, corresponding to a temperature coefficient of 0.88 per 10°C. The velocity of the formation reaction is of the same order as that which is catalyzed by animal charcoal in the dark, whether Uviol light or that from a quartz lamp is used.

Attempts to obtain sulfuryl bromide by the irradiation of sulfur dioxide and bromine have not been successful.[309]

Photochemistry of Miscellaneous Substances

Phosphine and Arsine. In the absorption spectrum of phosphine, Cheesman and Emeléus[310] observed poorly developed bands with centers at approximately 2315 and 2290A. Arsine and stibine showed only continuous absorption. In the photochemical decomposition of the latter, hydrogen was formed.

The mercury-sensitized decomposition of phosphine, as affected by variations in the partial pressures of phosphine, hydrogen, oxygen and argon, was investigated by Melville.[311] Collision of excited mercury atoms with phosphine was believed to produce H and PH_2. Recombination of these products by a wall reaction was indicated by the decrease in the reaction rate which was observed to follow an increase in the surface-to-volume ratio of the vessel. An observed inhibition by added hydrogen was attributed to the effect of the latter in deactivating the excited mercury atoms and to a wall reaction between the additional atomic hydrogen so produced and the phosphorus-containing intermediate. By attacking the intermediate, added oxygen increased the rate of the phosphine decomposition. That the oxide so formed initiated a stable chain reaction between the remaining phosphine and oxygen was shown by the acceleration of this reaction by argon.

The lowering of the explosion limit of phosphine-oxygen mixtures by mercury arc irradiation was shown to be due to a surface effect probably connected with the adsorption of hydrogen by the wall of the containing vessel. The direct photochemical decomposition of phosphine by the radiations from zinc or aluminum sparks leads to the formation of hydrogen and red phosphorus.[312]

Melville[313] also finds that at room temperature the absorption spectrum of phosphine consists of a region of continuous absorption beginning at 2300A, preceded by four diffuse bands. At 300°C., the bands disappear and the absorption limit moves toward longer wave-lengths. The direct photochemical decomposition has a quantum yield of 0.56 when conducted in a 7 cm. bulb and 0.49 in a 2 cm. bulb. It is independent of temperature below 300°. Atomic, but not molecular, hydrogen decreases the yield.

An oxygen-phosphine mixture reacts explosively between two sharply defined pressure limits. The lower one can be diminished by irradiation between the wave-lengths of 2500 and 2800A. The effect is ascribed to the formation of a small quantity of an active substance from the phosphine; this does not decay immediately when the elimination ceases.[314]

Melville and Roxburgh[315] found for the reaction produced by irradiation of an oxygen-phosphine mixture at 0.05 mm. a quantum yield of 200, a stable chain reaction occurring. Above the upper limit of irradiation for explosion in the photochemical oxidation of phosphine, the chain reaction is inhibited by oxygen.

[309] Trautz, M., *Z. Elektrochem.*, **21**, 329 (1915); Schwarz, R., and Kunzer, W., *Z. anal. Chem.*, **183**, 376 (1929).

[310] Cheesman, G. H., and Emeléus, H. J., *J. Chem. Soc.*, 2847 (1932).

[311] Melville, H. W., *Proc. Roy. Soc.*, **138A**, 374 (1932).

[312] Melville, H. W., *Nature*, **129**, 546 (1932).

[313] Melville, H. W., *Proc. Roy. Soc.*, **139A**, 541 (1933); Melville, H. W., and Bolland, J. L., [*Ibid.*, **160A**, 384 (1937)] and Melville, H. W., Bolland, J. L., and Roxburgh, L., [*Ibid.*, 406] also investigated mercury-sensitized exchange reactions of deuterium and phosphine and the decomposition of trideuterophosphine.

[314] Hinshelwood, C. N., and Clusius, K., *Proc. Roy. Soc.*, **129A**, 589 (1930).

[315] Melville, H. W., and Roxburgh, L. H., *J. Chem. Physics*, **2**, 739 (1934).

Since the continuous absorption of arsine begins at only 2390A, the sensitized decomposition produced by mercury atoms excited by the 2537A line may be studied without any complication due to a direct reaction.[316] Hydrogen gas and a film of arsenic are formed. The rate of decomposition is directly proportional to the intensity of the light and, at high pressures, is independent of the arsine pressure. At low pressures, the rate is decreased because the excited mercury atoms lose some of their energy by fluorescence. The decomposition is very slightly inhibited by addition of hydrogen. The quantum yield is 1.03.

Germane absorbs only in the very short wave-length region, probably at about 1700A. Absorption is entirely continuous at least as far as 1550A.[317] Radiations transmitted by very thin layers of quartz will decompose germane into hydrogen and germanium. The primary process is uncertain. A mercury-sensitized reaction also leads to the same products.[318]

A mercury-sensitized decomposition of silane to hydrogen and a solid SiH_x has been reported by Emeléus and Stewart.[319] The lack of absorption by this material prevents the occurrence of any direct photochemical decomposition. Mixtures of 30-50 per cent of silane with oxygen at low pressures explode when irradiated by the mercury resonance line, hot mercury spark, or aluminum spark. The process may be due to the formation of excited oxygen molecules. At higher pressures (100-500 mm.), the mixture reacts slowly after an induction period which depends on the initial pressure and oxygen concentration to give silicon. At the beginning the pressure increase is an exponential function of the time.

Siloxene, $Si_6O_3H_6$, reacts with organic halides in the presence of light to produce a monohalogenated siloxene.[320] Siloxene absorbs only light of short wave-length, but can be sensitized to long wave-lengths by the addition of a very small quantity of hydroxysiloxene or of a dye. Since colored products are formed as the reaction proceeds, there is also autosensitization.

Iron pentacarbonyl vapor can be decomposed by irradiation with the wave-length 4000A, with a quantum efficiency of two.[321] The reaction is inhibited by foreign gases. Eyber explained the results by assuming an excited molecule to react with a normal one with the production of carbon monoxide and the compound $Fe_2(CO)_9$. On the other hand, Thompson and Garratt[322] found the vapor to have continuous absorption beginning at 4100A. They suggested that the primary process involves a dissociation into CO and $Fe(CO)_4$. The latter then reacts with a molecule of the pentacarbonyl to give the observed product $Fe_2(CO)_9$. In hexane or carbon tetrachloride the continuum began at 5500A, but this was attributed to the presence of the decomposition product as an impurity. Eyber found that hexane solutions absorb strongly below about 4600A.

Both the vapor and hexane or carbon tetrachloride solutions of nickel tetracarbonyl show only continuous absorption, beginning at 3950A. The first reaction

[316] Simmons, N. L., and Beckman, A., *J. Am. Chem. Soc.*, **58**, 454 (1936).

[317] Mahncke, H. E., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **57**, 456 (1935).

[318] Romeyn, H., Jr., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **54**, 4143 (1932).

[319] Emeléus, H. J., and Stewart, K., *Trans. Faraday Soc.*, **32**, 1577 (1936). x is < 0.9. For disilane and trisilane decomposition, see Schwarz, R., and Heinrich, F., *Z. anorg. allgem. Chem.*, **221**, 277 (1935).

[320] Kautsky, H., and Thiele, H., *Z. anorg. allgem. Chem.*, **144**, 197 (1925); *Chem. Abs.*, **19**, 2313 (1925).

[321] Eyber, G., *Z. physik. Chem.*, **144A**; see also Warburg, O., *Naturwiss.*, **16**, 856 (1928).

[322] Thompson, H. W., and Garratt, A. P., *J. Chem. Soc.*, 525 (1934).

of irradiation is to produce carbon monoxide and nickel tricarbonyl, the latter further dissociating into carbon monoxide and nickel. In the gas phase, however, no change is observed,[323] a thermal recombination balancing the photochemical decomposition. The quantum efficiency is higher, 2.12, for solutions in carbon tetrachloride than for those in hexane or cyclohexane. The yield increases somewhat with frequency from a threshold value corresponding to the limit of continuous absorption. Fedorov and Talmud[324] find the reaction can be sensitized to wave-lengths greater than 6400A by pinacyanol. Webster[325] claims the polymerization of nickel carbonyl to $(Ni(CO)_4)_2$, which has antiknock properties when added to motor fuels, by the action of actinic light.

[323] Thompson, H. W., and Garratt, A. P., *J. Chem. Soc.*, 1817 (1934).

[324] Fedorov, F. P., and Talmud, D. L., *J. Phys. Chem. (U.S.S.R.)*, **8**, 789 (1936); *Chem. Abs.*, 31, 1702 (1937).

[325] Webster, H. G., U. S. P. 2,002,805, May 28, 1935; *Chem. Abs.*, **29**, 4932 (1935).

Chapter 20

Inorganic Reactions in Liquids

General Characteristics

In liquid phase reactions the photochemical mechanism may be altered because of the influence of neighboring molecules of the reactant if a pure liquid, or of the solvent if a solution, upon the molecule which absorbs a photon. These influences are exerted even during the act of absorption. As pointed out by Franck and Rabinowitsch,[1] the molecules in a liquid may be regarded as being permanently in a state of collision. As a result, collisions with adjacent molecules are occurring during the brief period between the absorption of a photon by a molecule and its dissociation (about 10^{-13} second). Such collisions may deactivate the excited molecule even before it has a chance to dissociate. Accordingly, the yield of the primary process might be expected to fall below unity. A lowered quantum yield in the primary process would be reflected also in a lowered quantum yield for the measured overall reaction. This consideration would apply to any photochemical process in which the primary act is the formation of an excited molecule.

Since all collisions between dissociation products would be triple collisions with solvent molecules, the occurrence of secondary recombination processes would be enhanced and contribute to a lowering of the quantum yield. Such processes would be true recombinations of the dissociation products of individual molecules rather than combinations of products of dissociation of different molecules or of products produced in secondary reactions. This follows because any excess kinetic energy with which atoms or free radicals may be endowed, by virtue of a dissociating photon of slightly shorter wave-length than corresponds to the energy required for dissociation, would be lost by collision before the products had moved much more than a molecular diameter. Recombination would then be possible if the products were still close together. When much shorter wave-lengths are used in irradiation, the kinetic energies of the dissociation products are great, enabling the latter to travel farther apart before losing this excess energy. The result would be a reduction of the chance of recombination and an increase in the quantum yield over that produced by the use of longer wave-lengths.[2]

In certain liquids and in solutions in non-polar solvents such as carbon tetrachloride, it is possible that the rates and temperature coefficients of secondary processes are not far different from those in the gaseous state.[3] In other cases there may be complications due to combinations of the solvent with the dissociation products of the primary process. Indeed, the original solute may be solvated

[1] Franck, J., and Rabinowitsch, E., *Trans. Faraday Soc.*, **30**, 129 (1934).

[2] Sveshnikov, B. Y., [*Acta Physicochim. U.R.S.S.*, **3**, 257 (1935)] has discussed the theory of the quenching of the fluorescence of excited molecules as dependent on the viscosity of the solvent. He has also considered the effect the concentration of a reactant which does not require activation may have on the mean life of excited molecules. *Compt. rend. acad. sci. U.R.S.S.*, **15**, 177 (1937); *Chem. Abs.*, **31**, 656 (1938). Note also Schpolski, E., *Acta Physicochim. U.R.S.S.*, **3**, 255 (1935).

[3] Moelwyn-Hughes, E. A., "Kinetics of Reactions in Solution," p. 63. Oxford University Press, 1933.

and give rise to further complications. Details of effects exerted by the solvent upon secondary processes will be discussed in connection with individual reactions.

Dickinson [4] pointed out that as a result of these possibilities, reactions in the liquid phase might be expected to have quantum yields less than, or in some cases equal to but never greater than, those of the same reactions in the gas phase. He examined the reactions in which available data permitted a comparison of the yields in the two states. Of eleven reactions studied, ten exhibited yields in the liquid phase which were slightly less than those in the gas phase. An exception was the decomposition of ethyl iodide produced by absorption within the continuous spectral region. This halide, according to West and Ginsburg,[5] undergoes little decomposition in the gas phase and more in the liquid phase or in solution in hexane or benzene. Dickinson, however, raised the question as to whether the effects of traces of oxygen had been entirely eliminated in this work.[6]

Rollefson [7] has discussed cases in which the solute is affected by the solvent and, in particular, the influence of the solvent, especially if polar, upon photosensitization processes effected by such fluorescent substances as uranyl salts.

Absorption Spectra. Spectral evidence as to the nature of the primary process—dissociation, predissociation or formation of excited molecules—is rarely available for the interpretation of photochemical reactions in condensed systems. However, the products capable of secondary reactions will be dissociation products, for collisions would easily lead to the dissociation of excited molecules. The absorption spectra of liquids seldom exhibit the fine structure characteristic of transitions between rotational levels of molecules seen in the absorption of gases and the occurrence of which was used as a criterion of the absence of predissociation. Even the more widely separated bands characterizing the vibrational levels of molecules are usually but partially distinguishable. The blurring of the finer structure is in part attributable to the effect of collisions with neighboring molecules and in part to the Stark effect of the charges of the adjacent molecules. The effects of collision-broadening may be lessened by making the observations at liquid air temperatures in some cases. This is particularly to be observed in the case of crystals. For example, at very low temperatures (20°Abs.) sharp lines replace the broad absorption bands of potassium dichromate observable at ordinary temperatures.[8]

In other cases, as azobenzene, the broad bands seen at ordinary temperatures are broken into a series of narrow but still diffuse bands at −196°C., forming a line spectrum at 20°Abs.

Aside from the obliteration of the finer structure, the situation of the absorption region may be either unaffected or shifted to other wave-lengths by the presence of a solvent. Instances in which there is similarity in absorption in the gas phase and in liquid solution are found in the halogens as vapors or in solution in carbon tetrachloride, chloroform or carbon disulfide, and for hydrogen sulfide in water and in hexane. When the solute is solvated, there may, however, be

[4] Dickinson, R. G., *Chem. Rev.*, **17,** 413 (1935); *J. Phys. Chem.*, **42,** 739 (1938); see also Rollefson, G. K., and Libby, W. F., *J. Chem. Physics,* **5,** 569 (1937).

[5] West, W., and Ginsburg, E., *J. Am. Chem. Soc.*, **56,** 2626 (1934).

[6] For further discussion of the modifications of the quantum yield of the primary process which may occur in solution, see also Kistiakowsky, G. B., *Cold Spring Harbor Symposia Quant. Biol.*, **3,** 44 (1935), and Rabinowitsch, E., and Wood, W., *Trans. Faraday Soc.*, **32,** 1381 (1936).

[7] Rollefson, G. K., *Chem. Rev.*, **17,** 425 (1935); *Cold Spring Harbor Symposia Quant. Biol.*, **3,** 19 (1935); *Chem. Abs.*, **30,** 6648 (1936).

[8] Obreimow, I., and de Haas, W. J., *Proc. K. Acad. Wetensch. Amsterdam,* **31,** 353 (1928); Schaumann, H., *Z. Physik,* **76,** 106 (1932).

marked shifts in the situation and intensity of the absorption bands.[9] The effects of variation of temperature on the extinction coefficients of a number of salt solutions, mostly colored, have been measured by Mukerji, Bhattacharji and Dhar.[10] The changes are in large part attributed to changes in the hydration of the solutes, usually ions, at higher temperatures.

There have been many studies of the absorption spectra of salts in solution, the absorption of the solution being due in large part to absorption by the ions present. The influence of electrostatic forces upon the magnitudes of the extinction coefficients in various solutions and the effects of adding foreign non-absorbing salts have been investigated, but for present purposes it is sufficient to note that the effects of these electrostatic forces may be great enough to alter markedly the absorption region from that of the pure undissociated compound. The result may be that in solutions the photochemically effective wave-length regions may differ from those which induce the same reaction in the gas phase.[11] For example, the absorption band of the iodide ion found at 2273A in aqueous solution shifts toward shorter wave-lengths in concentrated calcium chloride solutions and in alcohol. Changes in the solvation of the ions are of importance in producing these effects.[12] Scheibe [13] has reviewed the causes of variations in the absorption spectra of solutions.

Cations of the alkalies and alkaline earths do not absorb light, and visible or ultraviolet absorption exhibited by solutions of their salts is usually due to the anions. Other cations, as those of the transitional group of elements, iron, chromium, copper, cobalt, nickel, or manganese, exhibit absorption believed to arise from low-energy electron shifts involving the incomplete electron shell in the structure of these atoms.[14]

Electron-Affinity Spectra. The spectra of the anions, particularly those of the halogens, have been called "electron affinity spectra," since it is considered that the electron held by the atom or radical as ion is driven off from it in the absorption process, rather than excited to a higher energy state.[15] The iodide ion exhibits two broad continuous bands with maxima at about 2250 and 1950A (see Figure 113). The separation between these maxima when expressed as the difference in the corresponding wave-numbers (about 8000 cm^{-1}.) is very close to the difference between the ground state and an excitation state of the iodine atom (7600 cm^{-1}.). Thus one maximum is interpreted as caused by separation of an electron from a normal iodine ion and the other to separation of an electron from an excited ion. The hydration of the ion and the hydration of the electron modify the results somewhat. Franck and Haber [16] have postulated that, as a part of the process, the electron attaches itself to an OH group split off from a molecule of hydration of the ion, a hydrogen atom being also formed. Similar considerations also apply to the spectra of other anions, but in the more complex ones, as the nitrate ion, other decomposition possibilities must also be considered. Farkas and Farkas modify the theory by assuming that the primary process involves a

[9] Hantzsch, A., and Carlsohn, H., *Z. anorg. Chem.*, **156,** 199 (1926).

[10] Mukerji, B. K., Bhattacharji, A. K., and Dhar, N. R., *J. Phys. Chem.*, **32,** 1834 (1928).

[11] von Halban, H., and Ebert, L., *Z. physik. Chem.*, **112,** 321 (1924); von Halban, H., *Trans. Faraday Soc.*, **21,** 620 (1926); von Halban, H., and Eisenbrand, J., *Z. physik. Chem.*, **122,** 337 (1926).

[12] Scheibe, G., with Römer, R., and Rössler, G., *Ber.*, **59B,** 1321, 2616 (1926).

[13] Scheibe, G., *Angew. Chem.*, **50,** 212 (1937).

[14] Saha, M., *Nature,* **125,** 130 (1930); Shibata, Y., and Harai, K., *J. Chem. Soc. Japan,* **56,** 1 (1935); Pestemer, M., and Bernstein, P., *Z. anorg. allgem. Chem.*, **223,** 121 (1935); Samuel, R., and others, *Z. physik. Chem.*, **22B,** 431 (1933); *Bull. Acad. Sci. United Provinces Agra Oudh, Allahabad,* **3,** 157 (1934); *Trans. Faraday Soc.*, **31,** 423 (1935); *Indian J. Physics,* **9,** 491 (1935); Inoue, T., *J. Chem. Soc. Japan,* **54,** 65 (1933); *Chem. Abs.*, **27,** 2382 (1933).

transfer of the electron from the anion to a water molecule in the hydration layers. If no photochemical change ensues, the electron returns to the initial state. If a reaction occurs, the final state is reached by the transfer of the electron to a positive ion. Thus,

$$(I^-.H_2O) + h\nu \longrightarrow I.H_2O^-$$
$$I.H_2O^- + (H^+) \longrightarrow I + H_2O + H.$$

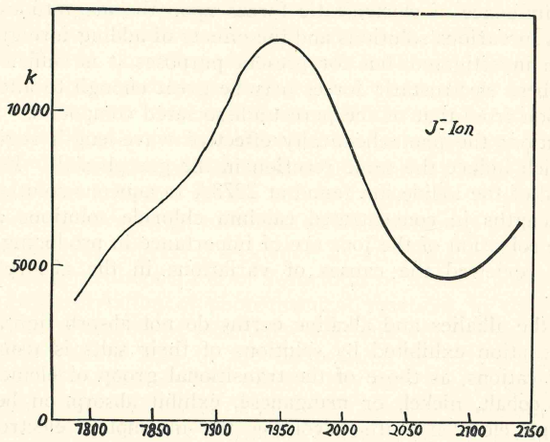


FIGURE 113. Electron Affinity Spectrum for Iodide Ion (Franck and Scheibe, *Z. physikalische Chemie*).

Lederle [17] concludes, as a result of measurements of the electron-affinity spectra of aqueous and alcoholic solutions of alkali and alkaline earth halides, that the effects of temperature and solvent may be satisfactorily explained by the hypothesis of Franck and Scheibe. The hydroxyl ion has an absorption maximum at 1860A.[18]

Since the theory of photochemical reactions in liquid systems is less advanced than is that of reactions in gaseous systems, the treatment of much of the material in this chapter is necessarily of a more descriptive and qualitative nature than that of the preceding chapter. On the other hand, photochemical processes in crystals, particularly the alkali and silver halides, are now being very actively studied from a theoretical standpoint.

WATER AND HYDROGEN PEROXIDE

Water is very transparent to ultraviolet wave-lengths greater than 1950A, but below this its transparency decreases rapidly.[19] Although earlier observers [20] had

[15] Franck, J., and Scheibe, G., *Z. physik. Chem.*, **4B**, 22 (1928); **5B**, 355 (1929); Fromherz, H., and Menschick, W., *Z. physik. Chem.*, **7B**, 439 (1930); Farkas, A., and Farkas, L., *Trans. Faraday Soc.*, **34**, 1113 (1938).

[16] Franck, J., and Haber, F., *Ber. Berl. Akad.*, 250 **(1931)**; Scheibe, G., *Z. Elektrochem.*, **35**, 701 (1929); *Sitzb. phys.-med. Soc. Erlangen*, 58-59 (1927); *Chem. Abs.*, **22**, 4371 (1928). See also Dutta, A. K., *Trans. Bose Research Inst., Calcutta*, **10**, 209 (1934-5); *Chem. Abs.*, **32**, 3263 (1938); Farkas, A., and Farkas, L., *Trans. Faraday Soc.*, **34**, 1113, 1120 (1938).

[17] Lederle, E., *Z. physik. Chem.*, **10B**, 121 (1930).

[18] Ley, H., and Arends, B., *Z. physik. Chem.*, **6B**, 240 (1929).

[19] Tsukamoto, K., *Rev. d'optique*, **7**, 89 (1928); for data throughout the visible see Hulburt, E. O., and Dawson, L. H., *J. Opt. Soc. Am.*, **24**, 175 (1934) and for sea water, Hulburt, E. O., *Ibid*, **17**, 15 (1928).

[20] Kernbaum, M., *Farm. Polsk.*, **16**, 71 (1913); *Chem. Abs.*, **8**, 387 (1914).

concluded that ultraviolet rays, and even the rays of the sun, would cause some decomposition of pure oxygen-free water, with the production of hydrogen peroxide, subsequent work has shown that only radiations of very short wave-length [21] (1900A) produce any effect. Tian states that if the water contains dissolved oxygen, this may react with the hydrogen set free in the primary decomposition to form hydrogen peroxide. Ozone, formed from oxygen, may further react with hydrogen peroxide.[22] Further work is needed.

It has been found by Bowden [23] that if, during the electrolysis of dilute sulfuric acid, the mercury cathode is irradiated by wave-lengths less than 4000A, there is a marked acceleration of the deposition of hydrogen. A similar effect occurs with respect to the liberation of oxygen at a platinum electrode, but the threshold wave-length was not determined.[24]

The sensitized formation of hydrogen peroxide in the presence of aqueous suspensions of zinc oxide (in contact with air) when exposed to sunlight has been described by Baur and Neuweiler,[25] who represent the process in terms of the "molecular electrolysis" theory of photosensitization discussed in Chapter 16. The yield was said to be greatly increased in the presence of small amounts of glycerol, dextrose or benzidine, these added substances being simultaneously oxidized. When glycerol was employed, there was an indication of the formation of dihydroxyacetone and possibly glycerose; with benzidine, a brown, insoluble oxidation product resulted. When the sensitizer was eosin or fluorescein rather than zinc oxide, the formation of hydrogen peroxide could be observed only when dextrose or benzidine, but not glycerol, was present.

The Decomposition of Hydrogen Peroxide. In solutions, the coefficients of absorption of hydrogen peroxide are the same as those for the vapor.[26] The absorption, which begins between 3700 and 3800A, is but slight to 3000A, after which it increases rapidly with decreasing wave-length. In Figure 112, the circles represent values for the solutions and the crosses those for the vapor. Sharma [27] concludes the abrupt termination of the absorption spectra of 3, 10 and 30 per cent solutions at 2055A to correspond to the dissociation $H_2O_2 + h\nu \rightarrow 2H + O_2$.[28] The progressive addition of alkali displaces the absorption curves toward longer wave-lengths, a limiting value of the shift (500A) being attained when the ratio of alkali to peroxide is one to one. The new absorption is attributed to the ion HO_2', the formation of which involves a change in the mode of interatomic linking.[29]

It was early found that the velocity of decomposition of hydrogen peroxide in dilute aqueous solution increases with increasing frequency of the radiation employed.[30] It has been observed that with dilute solutions of the peroxide, the velocity is dependent on the concentration.[31] Tian and also Henri and Wurmser

[21] Tian, A., *Compt. rend.*, **156**, 1063 (1913); Houben, J., and Fischer, W., *Arb. biol. Reichs. Land-Forstw.*, **15**, 601 (1928); *Chem. Abs.*, **23**, 2366 (1929); Coehn, A., *Ber.*, **43**, 880 (1910).

[22] See also Kernbaum, M., *Compt. rend.*, **149**, 273 (1929).

[23] Bowden, F. P., *Trans. Faraday Soc.*, **27**, 505 (1931).

[24] See also Audubert, R., *Compt. rend.*, **189**, 1265 (1929).

[25] Baur, E., and Neuweiler, C., *Helv. Chim. Acta*, **10**, 901 (1927).

[26] Urey, H. C., Dawsey, L. H., and Rice, F. O., *J. Am. Chem. Soc.*, **51**, 1371 (1929).

[27] Sharma, R. S., *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 51 (1934); *Chem. Abs.*, **29**, 7187 (1935).

[28] For a comparison with the absorption of mono- and di-alkyl peroxides, see Lederle, E., and Rieche, A., *Ber.*, **62B**, 2573 (1929).

[29] Bredig, G., Lehmann, H. L., and Kuhn, W., *Z. anorg. Chem.*, **218**, 16 (1934).

[30] Tian, A., *J. Chem. Soc.*, **108** (ii), 828 (1915); *J. Soc. Chem. Ind.*, **35**, 114 (1916); *Chem. Abs.*, **10**, 1960 (1916).

[31] Tian, A., *l. c.*; Kornfeld, G., *Z. wiss. Phot.*, **21**, 66 (1921); Henri, V., and Wurmser, R., *Compt. rend.*, **157**, 1261 (1913); **156**, 1012 (1913).

believed the velocity of decomposition to be proportional to the intensity of the incident radiation rather than to that absorbed. Qureshi and Rahman[32] state, however, that the rate is proportional to the square root of the light intensity. In recent observations, Kornfeld[33] concluded that in neutral solutions, the rate of decomposition produced by the 3110A line is proportional to the product of the concentration of hydrogen peroxide and the square root of the absorbed light. This relationship fails in acid solutions. This may have been a contributing factor in causing the divergent results of previous observers. Also Kornfeld noted that the quantum yield is variable and large, sometimes being as high as 80.

The presence of dust in the water used as solvent has been found to affect the results,[34] the rate of decomposition being roughly proportional to the dust content. Qureshi and Rahman found the quantum yield to vary with decreasing concentration between about seven and three, there being a maximum of eleven at a concentration of 0.09 M. Kornfeld proposed a chain mechanism for the reaction applicable in the presence of sodium sulfate and sulfuric acid:

$$H_2O_2 + h\nu \longrightarrow 2OH$$
$$H_2O_2 + OH \longrightarrow H_2O + HO_2$$
$$H_2O_2 + O_2 \longrightarrow O_2 + OH + OH$$
$$OH + O_2H \longrightarrow H_2O + O_2.$$

In neutral solutions longer chains might account for the higher yields. Heidt,[35] using light of high intensity at 3130A, found the quantum yield to approach unity as the concentration of the hydrogen peroxide was decreased to low values. As is usually the case with chain reactions, the decomposition is readily inhibited by traces of various substances. Henri and Wurmser observed this stabilizing action on hydrogen peroxide as early as 1913. Anderson and Taylor[36] noted that although many inhibitors might function by absorbing the effective rays, some of the most effective inhibitors did not absorb the destructive wave-lengths. Furthermore, the inhibitors in general acted much more effectively when placed within the solution than when employed as external light filters. Subsequent work on the susceptibility of chain processes to inhibitors has given a new conception of the action of the latter as efficient breakers of chains. This topic is discussed in somewhat greater detail in connection with the oxidation of sulfites, but for a more general treatment, the reader is referred to texts on the theory of chain reactions.[37]

Among the most efficient inhibitors for decomposition of hydrogen peroxide found by Anderson and Taylor were ethylamine, aniline, phenol and quinine salts. Strong to fairly strong inhibitors included methyl benzoate, benzamide and acetanilide. Moderate inhibitors were hydrocinnamic acid, ethyl cinnamate, methyl oxalate, ethyl alcohol and benzyl alcohol. Weak inhibitors included ethyl benzoate, ethyl phenylacetate, acetone, acetophenone, benzophenone and benzene. Acetic acid, ethyl acetate and acetamide had little or no effect. In most cases the concentrations of inhibitor employed ranged from 0.0001 to 0.005 per cent. Anderson and Taylor[38] concluded that inorganic bases are excellent inhibitors, inorganic acids are good inhibitors, bromides and chlorides have a moderate inhibitory action and other inorganic salts such as nitrites, sulfates and perchlorates, have no action. They found also that one hydroxyl ion inhibits as much as 25 hydrogen ions and that inhibition has a zero temperature coefficient.

[32] Qureshi, M., and Rahman, M. K., *J. Phys. Chem.*, **36**, 664 (1932).
[33] Kornfeld, G., *Z. physik. Chem.*, **29B**, 205 (1935).
[34] Rice, F. O., and Kilpatrick, M. L., *J. Phys. Chem.*, **31**, 1507 (1927).
[35] Heidt, L. J., *J. Am. Chem. Soc.*, **54**, 2840 (1932).
[36] Anderson, W. T., Jr., and Taylor, H. S., *J. Am. Chem. Soc.*, **45**, 650 (1923).
[37] Semenoff, N., "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935.
[38] Anderson, W. T., Jr., and Taylor, H. S., *J. Am. Chem. Soc.*, **45**, 1210 (1923); see also Mathews, J. H., and Curtis, H. A., *J. Phys. Chem.*, **18**, 521 (1914).

Recently, Dain and Shvartz[39] concluded that the photochemical decomposition is defined by the rate equation:

$$-d(H_2O_2)/dt = kI^{1/2}(H_2O_2)^{1/2}.$$

At 75° and under irradiation by a mercury vapor lamp, the rate of decomposition is reduced to one-half by the addition of 91×10^{-4} mole per liter of dimethyl ketone, of 20×10^{-4} of methyl ethyl ketone, or of 26×10^{-4} of diethyl ketone. The correction for the internal absorption of light by the ketone was never over 5 per cent. The ratios of the velocities of the inhibited and uninhibited reactions are linear functions of the ketone concentration. They believe the ketones decrease the initial number of chains, rather than break those already formed.

The well-known catalytic activity of lead peroxide and of platinum in the thermal decomposition of hydrogen peroxide is said to be increased by previously exposing the catalysts to ultraviolet light.[40] Irradiation during thermal decomposition increases the activity of graphite, charcoal and lead peroxide as catalysts, but may decrease that of platinum. It is suggested that electrons are transferred from hydrogen peroxide molecules adsorbed on inactive regions of the catalyst to those on active centers.

Sensitization of the decomposition of hydrogen peroxide to visible light has long been known. Kistiakowsky,[41] who used as sensitizer a mixture of potassium ferro- and ferricyanides, found the decomposition to follow a monomolecular course and to continue after the irradiation had ceased. According to Weigert,[42] potassium ferrocyanide which has been irradiated will cause a reaction when added to hydrogen peroxide in the dark. The same phenomenon has been found also in the case of sodium nitroprusside by Qureshi,[43] who believes the irradiation of this compound produces some colloidal Prussian blue which may serve as a catalyst for the dark reaction.

The quantum yield for the bromine-sensitized reaction has been found by Livingston and Schoeld[44] to be less than unity, but Griffith and McKeown[45] find the yield much greater than one in blue light. They also deny the existence of a "photo-stationary" state in this system.

Notwithstanding the fact that the decomposition of hydrogen peroxide is so sensitive to dust, inhibitors and sensitizers, the reaction has been employed in actinometry by Koeppe.[46] However, Sostmann[47] found this method of measuring radiations unreliable.

[39] Dain, B. Y., and Shvartz, A. S., *Acta Physicochim. U.R.S.S.*, **3**, 291 (1935); *J. Phys. Chem. (U.S.S.R.)*, **7**, No. 2 (1936); *Chem. Abs.*, **30**, 2109 (1936).
[40] Pisarshevskiĭ, L. V., Korabel'nik, R. K., and Rinskaja, E. S., *Bull. Acad. Sci. U.R.S.S.*, **7**, 931 (1934); *Brit. Chem. Abs.* **A**, 47 (1935); *Chem. Abs.*, **29**, 2433 (1935).
[41] Kistiakowsky, G. B., *Z. physik. Chem.*, **35**, 431 (1901).
[42] Weigert, F., *Ann. Physik*, **24**, 261 (1907).
[43] Qureshi, M., *J. Phys. Chem.*, **35**, 656 (1931).
[44] Livingston, R., and Schoeld, E. A., *J. Am. Chem. Soc.*, **58**, 1244 (1936).
[45] Griffith, R. O., and McKeown, A., *J. Am. Chem. Soc.*, **58**, 2556 (1936).
[46] Koeppe, H., *Arch. Kinderheilk.*, **89**, 26 (1929-30).
[47] Sostmann, H., *Strahlentherapie*, **51**, 359 (1934); *Chem. Abs.*, **29**, 1012 (1935).

Photochemistry of the Halogens and Alkali Halides

The decomposition of 0.08 to 1.16 molar solutions of hydrogen iodide in hexane by a spark follows Einstein's law.[48] At the higher concentration, the quantum yield was, as in the gas phase, two. At lower concentrations, it dropped to one because the hydrogen and iodine atoms liberated by absorption may recombine as a result of collisions with the solvent molecules which carry off the excess energy. But in aqueous solutions, the specific photochemical yield, that is, the number of molecules decomposed per gram calorie absorbed, decreased with the use of increasing wave-lengths. This is contrary to the Einstein law, since at longer wave-lengths a constant amount of energy is divided between a greater number of smaller quanta and should, therefore, bring more molecules into reaction. Furthermore, the yields decreased rapidly as the concentrations of the aqueous solutions were decreased. In highly concentrated aqueous solutions (7.5 normal) the shortest wave-length used (2070A) gave an apparent quantum yield greater than two. To explain this it was suggested that an activated hydrogen iodide molecule might react with several consecutive normal molecules. Warburg believed also that the iodide ion forms no free iodine when irradiated, any production of iodine resulting from a decomposition of hydrogen iodide molecules. This explanation is not in line with the theory of complete dissociation of strong electrolytes. The anomalous effect of the wave-lengths was assumed due to the existence of hydrates of hydrogen iodide, since in hexane solutions the behavior was normal with respect to wave-length.

Subsequent to the development of the Franck and Haber theory of the primary process of absorption by halogen ions, $I^-(H_2O)+h\nu \rightarrow I+H+OH^-$ it became evident that the low yields in dilute solution may be explained as due to a combination of the hydrogen and iodine atoms which result from this process. The resulting hydrogen iodide then dissociates into hydrogen ions and iodide ions, the former combining with the hydroxyl ion formed in the primary process to yield water. In this way the original system present before the absorption of light is restored. In higher concentrations, the mechanism of the primary process, contrary to the assumption of Warburg, remains the same. In this case, however, there are present so many $I^-(H_2O)$ ions that the hydrogen atoms produced in the primary process may collide with the hydrated ions (rather than with iodine atoms) to produce a second iodine atom, an hydroxyl ion and a hydrogen molecule. The two iodine atoms may then combine to form a molecule of iodine. In this way, the quantum yields increase with the concentration to a value of about two as in the gas phase reaction.[49]

Butkov[50] studied the effect of various wave-lengths upon half-normal solutions of caesium, potassium and sodium iodides, and also upon more dilute solutions of the latter salt ($N/50$). He found that spark lines longer than 2700A failed to cause liberation of free iodine, this wave-length agreeing with the beginning of the absorption band of the iodide ion. Various shorter wave-length lines, notably the 2573A line, were effective in liberating iodine. In accordance with the Franck-Haber mechanism, the solutions in which iodine was liberated became more alkaline. The quantum yields in these experiments were, however, lower than those of Warburg and Rump in stronger hydrogen iodide solutions. Butkov placed the limit for the reaction in bromides, in which the yields of free bromine were lower, between 2265 and 2313A. He was unable to detect the liberation of chlorine from chlorides, the absorption of the chloride ion being located at wave-lengths shorter than 1900A.[51]

[48] Warburg, E., and Rump, W., *Z. Physik*, **47**, 305 (1928).

[49] Compare Farkas, A., and Farkas, L., *Trans. Faraday Soc.*, **34**, 1120 (1938). They were particularly concerned with the separation of hydrogen isotopes, when heavy water was in the solvent.

[50] Butkov, K., *Z. Physik*, **62**, 71 (1930).

Oxidation of Iodides. Earlier observations of the liberation of iodine from solutions of potassium iodide were in most cases complicated by photo-öxidations, since oxygen was rarely excluded from the solutions.[52] The influence of oxygen upon the photochemistry of potassium iodide has been shown quantitatively by Krauss and Bruchhaus.[53] An oxygen-containing solution on irradiation gave 4.92 per cent decomposition, but a similar solution previously boiled to remove the air, gave only a 0.76 per cent separation of iodine.

In testing the ability of variously colored glass bottles to protect drugs from the action of light, Jermstad and Østby[54] employed a 2-per cent potassium iodide solution to which had been added 4 per cent of dilute sulfuric acid. This was exposed in the bottles to be tested for one-half hour to a quartz lamp or for one hour to sunlight. A maximum separation of 1.5 mg. of iodine after this time was considered permissible. Black, red and all-brown glasses were satisfactory, although the latter gave 1.10 mg. of iodine in ultraviolet light or 0.50 mg. in sunlight. It is difficult to understand which components of the solution can absorb the wave-lengths available in such experiments, unless it might be the tri-iodide ion. It has been stated that even in darkness, hydrogen ions can catalyze oxidation to some extent.

Stobbe and Steinberger[55] found irradiation of alkaline solutions of potassium iodide in quartz or Uviol vessels to sunlight or the quartz mercury arc to cause a diminution of the alkalinity, probably because of the absorption of carbon dioxide from the air. If the solutions were originally but slightly alkaline, irradiation produced free iodine and hypoiodide. If the alkalinity was somewhat greater, iodate appeared also. In strongly alkaline solutions, the iodate was the only product. In neutral solutions there was but little reaction, but the addition of increasing amounts of carbon dioxide increased the photolysis through a maximum. The oxidation of neutral iodide solutions is a bimolecular reaction. The velocity coefficient is dependent on the wave-length and intensity of the light absorbed. It increases with time until so much tri-iodide ion has formed that the absorption of all available radiation is complete.

According to Berthoud and Nicolet,[56] the oxidation of hydriodic acid by oxygen in red light has a velocity which can be expressed by

$$\frac{d\,[I^-_3]}{dt} = k(KI)^x(O_2)\sqrt{I_0(I_3^-)\,(H_2SO_4)}$$

[51] Extensive data on the absorption of liquid hydrogen chloride and concentrated hydrochloric acid solutions have been given by Tréhin, R., *Compt. rend.*, **191**, 774 (1930); **193**, 1089 (1931); **195**, 1269 (1932); **199**, 1047 (1934); **200**, 1663 (1935); *J. Phys. Radium*, **4**, 449 (1933). Data for a number of chlorides are included and indicate that in concentrated solutions these are not as transparent to the region 2170 to 2500A as had been assumed from measurements on more dilute solutions. See also Hüttig, G., and Kükenthal, H., *Z. Elektrochem.*, **34**, 14 (1928) and Hantzsch, A., *Ber.*, **59B**, 1096 (1926). For earlier data, Getman, F. H., *J. Phys. Chem.*, **29**, 853 (1925), and Brannigan, P. J., and Macbeth, A. K., *Chem. Abs.*, **11**, 313 (1917). In the presence of free halogen, the absorption is altered because of the formation of trihalogen ions. Similar behavior is also encountered in alcoholic solutions, according to Job, P., *Compt. rend.*, **182**, 632, 1631 (1926).

[52] Suryanarayana, K., *J. Sci. Assoc. Maharajah's College, Vizianagaram*, **2**, 12 (1924); *Chem. Abs.*, **18**, 3548 (1924); Ross, W., *J. Am. Chem. Soc.*, **28**, 788 (1906); Kailan, A., *Monatsh.*, **34**, 1225 (1913); *Chem. Abs.*, **8**, 14 (1914).

[53] Krauss, F., and Bruchhaus, E., *Z. anorg. allgem. Chem.*, **189**, 53 (1930); *Brit. Chem. Abs.*, **A**, 553 (1930); earlier experiments were due to Plotnikow, J., *Z. physik. Chem.*, **58**, 214 (1907).

[54] Jermstad, A., and Østby, O., *Arch. Pharm. Chem.*, **92**, 463 (1935); *Chem. Abs.*, **29**, 7599 (1935).

[55] Stobbe, H., and Steinberger, F. K., *Z. anorg. Chem.*, **161**, 21 (1927).

In blue light, the velocity also increases as the square root of the light intensity. The photochemical reaction has a very small temperature coefficient, which Vita [57] believes depends in some manner upon the wave-length.[58] The influence of the presence of potassium dichromate and eosin in causing the separation of iodine from potassium iodide when illuminated has been studied by Reychler.[59]

The conductance of solutions of sodium iodide or of lithium bromide in acetophenone, but not of the solvent itself, decreases to a constant value when the solutions are exposed to light, and is restored to its former value when the solutions are returned to darkness.[60] A yellow color also appeared during irradiation. These results were confirmed by Morgan, Lammert and Crist,[61] who found also that solutions which had reached a constant conductance in glass would show a further decrease when placed in quartz vessels. The acetophenone is also decomposed with the formation of some benzoic acid. The quantity of iodine liberated from sodium iodide under these conditions was independent of the concentration of the salt, but depended upon the intensity of the radiation and the time of exposure, that is, upon the amount of acetophenone which had been decomposed.

The oxidation of ferrous ions by iodine, $2Fe^{++} + I_3 \rightarrow 2Fe^{+++} + 3I'$, was found to be photosensitive [62] in both the ultraviolet and the visible region of 5500 to 6500A (maximum at 5800A). Iodine, being present as the tri-iodide ion, was the photosensitive component of the solution, the iron salts or the iodide ion being practically inactive in the spectral regions employed. The temperature coefficient of the reaction is 1.17. From that of the dark reaction (2.71), it appeared that the energy of activation, 2.14 volts, was very close to a resonance potential of the iodine molecule (2.34 v.). For the wave-length 5790A, the quantum yield was found to be unity, one molecule of iodine reacting per absorbed quantum. Kistiakowsky [63] found this quantum yield given also by the wave-lengths 5460A, 4360 and 3660A, regions which Rideal and Williams had found ineffective. This absence of a maximum sensitivity at 5800A lessens the significance of the relation between the energy of activation and a critical potential of iodine noted by Rideal and Williams. By working with very dilute solutions at 0°C., and using light of wave-lengths greater than 5000A which had been freed from infrared rays, Ravitz and Dickinson [64] were able to show that, in the first stages of irradiation, light caused a reduction of the ferric ion by the iodide ion.

Mukerji and Dhar [65] found the reactions between iodine and such compounds as potassium formate, oxalate, ferrous sulfate and sodium nitrite to be accelerated principally by light in the range 3160 to 4600A. The quantum yields, calculated for 3880A, were low in the case of potassium oxalate, ferrous sulfate and sodium nitrite since for the transformation of each molecule of iodine there were required

[56] Berthoud, A., and Nicolet, G., *Helv. Chim. Acta*, **10**, 475 (1927); van Strachow, N., *Z. wiss. Phot.*, **18**, 267 (1919); *Chem. Centrbl.*, **90** (III), 309 (1919).

[57] Vita, N., *Gazz. Chim. Ital.*, **63**, 211 (1933).

[58] For comparisons of the kinetics of the photoxidation of the iodides of hydrogen and deuterium, see Cook, G. A., and Bates, J. R., *J. Am. Chem. Soc.*, **57**, 1775 (1935).

[59] Reychler, A., *Bull. Soc. Chim. Belg.*, **34**, 236 (1925); *Chem. Abs.*, **20**, 545 (1926). See also Winther, C., *Z. physik. Chem.*, **A174**, 41 (1935) and Tappeiner, H., *Chem. Centr.*, I, 1793 (1906); *Arch. klin. Med.*, **86**, 478.

[60] Dutoit, *Z. Elektrochem.*, **12**, 642 (1906); Nicollier, *Thesis*, Lausanne, 1907.

[61] Morgan, J. L. R., Lammert, O. M., and Crist, R. H., *J. Am. Chem. Soc.*, **46**, 1170 (1924).

[62] Rideal, E. K., and Williams, E. G., *J. Chem. Soc.*, **127**, 258 (1925); for previous observations, Sasaki, N., *Z. anorg. Chem.*, **122**, 61 (1922).

[63] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 976 (1927).

[64] Ravitz, S. F., and Dickinson, R. G., *J. Am. Chem. Soc.*, **53**, 3381 (1931).

[65] Mukerji, B. K., and Dhar, N. R., *Z. Elektrochem.*, **31**, 621 (1925); Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **196**, 26 (1931).

28, 15 and 49 quanta, respectively. In later work, Bhattacharya and Dhar [66] stated that the quantum yield in the reaction with sodium nitrite varies greatly at different temperatures and with different wave-lengths. The dark reaction is bimolecular and has a temperature coefficient of 2.7, that of the light reaction varying from 2.07 at 4725A to 2.35 at 8500A.

According to Batley,[67] the maxima observed in the absorption of alcoholic solutions of iodine at 3600 and 2900A are due to the formation of HI_3. When isolated in the solid form on gelatin, this has a maximum at 3680A. The true iodine curve, determined in the presence of ozone which decomposed the hydrogen iodides, shows only one maximum at 4770A and general absorption in the far ultraviolet. Formation of the hydrogen iodides is attributed to a slow photochemical reaction $C_2H_5OH + I_2 \rightarrow CH_3CHO + 2HI$, followed by an instantaneous reaction $I_2 + HI \rightarrow HI_3$.

Terenin [68] has studied the photochemical changes which occur in a layer of iodine molecules adsorbed on thallium iodide. Light, particularly of wave-length 5600A, produces a discoloration attributed to photodissociation of adsorbed molecules. The liberated iodine atoms are then bound by thallium ions. The presence of adsorbed hydrogen or oxygen molecules on the surface causes marked shifts of the wave-lengths which are active, but nitrogen has no effect. The results are ascribed to photochemical reactions between adsorbed iodine and hydrogen or oxygen, with the formation of hydrogen iodide and of iodine oxide.

Potassium iodate, when irradiated by short wave-lengths in a solution saturated with carbon dioxide, liberates iodine at a rate which is linear so long as the amount liberated is small compared with the total amount present as iodate.[69] In the presence of air, the rate of the reaction decreases slowly with time. When the solution is kept saturated with oxygen, iodine is not liberated. Carbon dioxide greatly increases the rate of photolysis.

Bromine. Bovis [70] finds bromine in water, carbon tetrachloride, chloroform or alcohol to show two absorption maxima of which one lies at 4100A and the other at 2600A. Since only the former is also exhibited by gaseous and by liquid bromine, the band at 2600A must be characteristic of bromine in solution.

Photochemical reaction between bromine and water appears to follow the reactions: [71]

$$Br_2 + H_2O \longrightarrow H^+ + Br' + HOBr$$
$$HOBr + h\nu \longrightarrow H^+ + Br' + 1/2O_2$$

The rate decreases with increasing bromide-ion concentration.

In light of wave-length 4360A, carbon tetrabromide is oxidized when present in concentrations above 0.05 mole per liter.

$$2CBr_4 + O_2 \longrightarrow 2COBr_2 + 2Br_2$$

At lower concentrations, the oxygen consumption is greater. The quantum yield is less than one. The reaction is accelerated by oxygen, retarded by bromine and

[66] Bhattacharya, A. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **7**, 709 (1930); *Chem. Abs.*, **25**, 251 (1931).

[67] Batley, A., *Trans. Faraday Soc.*, **24**, 438 (1928); *cf.* also Rabinowitsch, E., and Wood, W. C., *Ibid.*, **32**, 547 (1936).

[68] Terenin, A., *Acta Physicochim, U.R.S.S.*, **1**, 178, 407 (1934); *Chem. Abs.*, **29**, 685, 7810 (1935). *Brit. Chem. Abs.*, **A**, 943 (1935).

[69] Mathews, J. H., and Curtis, H. A., *J. Phys. Chem.*, **18**, 641 (1914); *J. Chem. Soc.*, **106** (ii), 830 (1914).

[70] Bovis, P., *Compt. rend.*, **185**, 57 (1927).

[71] Pagel, H. A., and Carlson, W. W., *J. Phys. Chem.*, **40**, 613 (1936).

unaffected by bromophosgene.[72] The suggested mechanism involves the primary removal of a bromine atom, which requires at most 50 kcal. The resulting CBr_3 then reacts with the oxygen.

Bromine oxide, Br_2O, prepared by the interaction of mercury oxide and bromine in carbon tetrachloride solution, decomposes in light by the following two reactions:[73]

$$Br_2O \longrightarrow Br_2 + 1/2O_2$$
$$Br_2O + CCl_4 \longrightarrow COCl_2 + Br_2 + Cl_2.$$

The maximum rate of decomposition of bromine chloride in the light is four times that in the dark. The quantum yield is of the order of a thousand.[74]

Chlorine. That sunlight decomposes chlorine water with the formation of oxygen and chlorides, or under certain circumstances, of chlorites and chlorates, has long been known. The loss of active chlorine in bleaching solutions in daylight has been found to be after 70 days in filled white glass bottles, 48 to 61 per cent, in half-filled bottles, 63 to 76 per cent and in half-filled brown bottles, 11 to 29 per cent.[75]

Free hypochlorous acid is said to be less sensitive to light than the sodium salt.[76] Sunlight, diffused daylight and the lines at 3130, 3650 and 4360A, appeared equally effective.[77] Despite repeated and detailed investigations, the interpretation of the reaction is not yet entirely clear. Neither hydrogen peroxide nor perchloric acid is formed, the only reaction products being hydrochloric acid, oxygen and chloric acid. To determine whether chlorine, hypochlorous acid or its ion is the photosensitive substance, Allmand and co-workers studied the effects on the rate and products formed, of the addition of various salts which might shift the equilibrium in the irradiated solutions. From the retarding effects of chlorides[78] or hydrochloric acid and the accelerating effects of buffer salts, they concluded that hypochlorous acid plays a more important part in the primary process than chlorine. The latter could not, however, be excluded, so that it was necessary to conclude that there may be two independent primary processes and two reaction mechanisms. In one at least, atomic oxygen was regarded as a primary product which, reacting with hypochlorous acid, produced chloric acid. When chlorine water was irradiated with a filtered band of mean wave-length 3650A, the quantum yield was approximately two. This was greatly decreased by the addition of hydrochloric acid (to 0.054 in 0.6*N* HCl). They believed an analysis of their data permitted an estimation of the quantum yield of the primary process (as distinguished from that of the overall reaction) as approximately unity. The temperature coefficient of the overall reaction was given as 1.4 by Benrath and Tuchel.[79]

The decomposition of sodium hypochlorite in neutral or alkaline solutions by wave-lengths in the range 4360-2130A was found to follow a monomolecular course

[72] Koblitz, W., Meissner, H., and Schumacher, H. J., *Ber.*, **70B**, 1080 (1937).

[73] Brenschede, W., and Schumacher, H. J., *Z. physik. Chem.*, **29B**, 356 (1935).

[74] Brauer, G., and Victor, E., *Z. Elektrochem.*, **41**, 508 (1935).

[75] Tuenter, J. P. A., *Chem. Weekblad*, **32**, 429 (1935); *Chem. Abs.*, **30**, 28 (1936); see also, Fowler, *J. Chem. Soc.*, **94**, (II), 914 (1908); Kling, A., and Schmutz, R., *Compt. rend.*, **192**, 1655 (1931) and Jacquemaine, R. P., and Doll, J. H., *Bull. Soc. Chim.*, **2**, 1669 (1935); *Brit. Chem. Abs.*, **A**, 1331 (1935).

[76] Bonnet, L., *Rev. gen. mat. color.*, **39**, 29 (1935); *Chem. Abs.*, **29**, 2312 (1935).

[77] Allmand, A. J., Cunliffe, P. W., and Maddison, R. E. W., *J. Chem. Soc.*, **127**, 655, 822 (1925).

[78] See, however, Shilov, E. A., and Kupinskaya, G. V., *Byull. IvNITI*, **12**, No. 6, 39 (1936); *Chem. Abs.*, **31**, 3288 (1937).

[79] Benrath, A., and Tuchel, H., *Z. wiss. Phot.*, **13**, 383 (1913).

by Lewis.[80] Allmand and Webb[81] found the proportion of sodium chlorate formed (40 to 53 per cent) to be independent of the intensity of illumination, hypochlorite concentration (0.08 to 0.01 molar) and of the concentrations of chloride, sulfate and free alkali. At higher dilutions, the yield of chlorate diminished. However, the yield of the latter increased with frequency of the light. The quantum yield was about unity at 3650A, slightly higher, 1.2, at 3130A and much higher, 4.7, at 2540A. The addition of electrolytes had an effect opposite to that previously noted in the case of hypochlorous acid or chlorine water. Thus, sodium chloride increased the quantum yield.

Chlorine Monoxide. Bowen stated that light (4100-4700A) acting on chlorine monoxide in carbon tetrachloride solution[82] caused formation of chlorine and oxygen. The quantum efficiency was calculated to be 0.81 to 1.02, on the assumption that these were the only products formed. In later work, however, Bowen observed that in the gaseous state two molecules of chlorine monoxide were decomposed by each absorbed quantum.[83] In the decomposition of chlorine monoxide in solution chlorine dioxide appears in appreciable amounts in comparison with the amount of monoxide decomposed, according to Dickinson and Jeffreys.[84] Using a method devised to eliminate the effects of the chlorine dioxide formed, they found that in solutions 0.014 to 0.054 molal in chlorine monoxide, the initial yield of chlorine dioxide is about 0.35 molecule per quantum absorbed. The initial rate of the decomposition of the chlorine monoxide has a quantum yield of at least 1.8. In a given run, the amount of the dioxide formed increases less and less rapidly with the number of quanta absorbed as the exposure is prolonged. This is possibly because the dioxide acts itself as an internal filter and also because it is also subject to photochemical decomposition.

Chlorine Dioxide. The decomposition of chlorine dioxide in carbon tetrachloride solutions (0.0346 to 0.317 molar) by blue and violet light was believed by Bowen[85] to have a quantum efficeincy of unity. A repetition of this work by methods[86] which also took into account the rapid dark reaction,[87] changed this value to two when the 4150A line was employed. The initial concentrations were 10.4 to 33.3 millimoles of chlorine dioxide per liter. Filters were used to limit the light to 4100 to 4200A. The filters were 30 mm. of a solution of 5.5 per cent of cobaltous sulfate (7 H_2O) and 8 per cent of ammonium thiocyanate and 30 mm. of a solution containing 25 per cent of copper sulfate (5 H_2O) and 0.04 per cent of quinine sulfate.

Since this radiation falls in the banded region of the spectrum of gaseous chlorine dioxide, it was assumed that activated molecules are formed. These on collision with the solvent molecules suffer decomposition by one of the following schemes:

$$ClO_2 \longrightarrow Cl + O_2$$
$$ClO_2 \longrightarrow ClO + O$$
$$ClO_2 \longrightarrow Cl + O + O.$$

[80] Lewis, W. C. McC., *J. Chem. Soc.*, **101**, 2371 (1912); Spencer, L., *Ibid.*, **105**, 2565 (1914).

[81] Allmand, A. J., and Webb, W. W., *Z. physik. Chem.*, **131**, 189 (1928).

[82] Bowen, E. J., *J. Chem. Soc.*, **123**, 1199 (1923).

[83] Bowen, E. J., *J. Chem. Soc.*, **123**, 2330 (1923).

[84] Dickinson, R. G., and Jeffreys, C. E. P., *J. Am. Chem. Soc.*, **52**, 4288 (1930). It had, indeed, been observed to form in the gas phase reaction by Kistiakowsky, G. B., and Bodenstein, M., [*Z. physik. Chem.*, **116**, 371 (1925)], who believed the amounts small enough not to interfere with quantum yield measurements.

[85] Bowen, E. J., *J. Chem. Soc.*, **123**, 1199 (1923).

[86] Nagai, Y., and Goodeve, C. F., *Trans. Faraday Soc.*, **27**, 508 (1931).

[87] Luther, R., and Hoffmann, R., *Z. physik. Chem. Bodenstein-Festband*, 755 (1931).

It was believed that both of the two latter modes of decomposition required greater amounts of energy (80-85 kcal. for the second and 119 kcal. for the third) than is available at 4150A (69 kcal.). The first reaction is endothermic to the extent of only 2 kcal. For this reason the proposed mechanism which accounts for the yield of two, is

$$ClO_2 + h\nu \longrightarrow ClO_2^*$$
$$ClO_2^* (+ CCl_4) \longrightarrow Cl + O_2 (+CCl_4) + 67 \text{ kcal.}$$
$$Cl + ClO_2 \longrightarrow Cl_2O_2 + 56 \text{ kcal.}$$

Bowen and Cheung [88] found the quantum yield to increase from one at 4360A to two at 4050A or shorter wave-lengths. In aqueous solutions, the rate of photo-decomposition was found proportional to the light intensity and the quantum yields were lower, being 0.2 at 4360A and unity at 3000A. Chlorine, chloride ion, and chlorate ions were identified. It was suggested that in solution, chlorine dioxide undergoes predissociation at lower energy values than it does as a gas.

In stable solutions prepared by washing the chlorine dioxide solutions with weakly alkaline materials, Luther and Hoffmann [89] found, after a pre-exposure to light, a decomposition to occur in the dark at a rate proportional to the four-thirds power of the concentration of chlorine dioxide. They suggested that chlorine monoxide liberated during the exposure to light may have induced the dark reaction. They also observed that the photolysis in ultraviolet light is a reaction of zero order. Spinks and Taube [90] find relatively large amounts of chlorine hexoxide, chlorine heptoxide and chlorine monoxide to be formed in addition to chlorine and oxygen. For a bromine-sensitized decomposition by the line 5460A, the quantum yield is 0.2 to 0.3.

Chlorates. Oertel [91] found that under the action of ultraviolet rays the alkali salts of chlorates, bromates, iodates and periodates in aqueous solution decompose into oxygen and halogen quantitatively if the exposure is sufficiently prolonged. Only a very small decomposition could be observed in the case of perchlorates. The rate of decomposition of bromates was greater than that of iodates and that of iodates greater than that of chlorates. Suryanarayana [92] states that neutral potassium chlorate and potassium nitrate solutions liberate oxygen on exposure to ultraviolet, but that equilibrium is quickly established. Exposure of a mixture of potassium chlorate and iodide with exclusion of oxygen leads to the oxidation of the iodide.

Solid potassium chlorate evolves oxygen when irradiated by radiations of wave-lengths shorter than about 2800A.[93] The decomposition may also be brought about by the impact of 22-volt electrons, but those of lower voltages corresponding with 2800A could not be shown to be effective. According to Krishnan and Narayana-swamy,[94] photodissociation of the crystals shows an anisotropic effect, linearly polarized light producing a greater effect when the electric vector is in the plane of the chlorate ion than when it is along the normal to this plane.

[88] Bowen, E. J., and Cheung, W. M., *J. Chem. Soc.*, 1200 (1932).
[89] Luther, R., and Hoffmann, R., *Z. physik. Chem.*, **117A**, 17 (1936).
[90] Spinks, J. W. T., and Taube, H., *J. Am. Chem. Soc.*, **59**, 1155 (1937); *Can. J. Research*, **15B**, 499 (1937); *Chem. Abs.*, **32**, 2028 (1938).
[91] Oertel, W., *Biochem. Z.*, **60**, 480 (1914); *J. Chem. Soc.*, **106** (ii), 321 (1914).
[92] Suryanarayana, K., *J. Assoc. Maharajah's College, Vizianagaram*, **2**, 12 (1924); *Chem. Abs.*, **18**, 3548 (1924).
[93] Meiler, J. G., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **52**, 527 (1930).
[94] Krishnan, K. S., and Narayanaswamy, L. K., *Current Sci.*, **3**, 417 (1935); *Brit. Chem. Abs.*, **A**, 682 (1935).

Mack [95] has stated that chlorates may be electrolytically oxidized to perchlorate in an acid solution in the presence of oxygen activated by ultraviolet rays.

Fluorine Oxide. This compound absorbs ultraviolet light, but according to v. Wartenberg and Klinkott [96] is not decomposed by it. Palmer [97] finds that light from a hydrogen discharge tube on passing through a fluorite window into air at atmospheric pressure, caused the formation of a film on the outside of the window and upon this film a white powder. The film with metallic luster is soluble in alcohol and is probably calcium oxyfluoride. The powder, which forms more rapidly in moist air, is insoluble in water, but soluble in dilute hydrochloric acid.

Compounds of Nitrogen

Ammonia. Pure liquid ammonia begins to absorb at about 2500A, the absorption increasing rapidly and being complete at about 2350A. The absorption also increases as the temperature rises, the threshold for absorption changing from 2320A at −78° to 2580A at 26°C. In aqueous solutions absorption increases with concentration, but is always less than that of the same number of ammonia molecules in the liquid or gaseous state.[98]

No reaction occurs when pure liquid ammonia is exposed to the wave-length 2300A, although this radiation is capable of causing the decomposition of gaseous ammonia.[99] Similarly, in water solution, the yield is kept low by recombination in triple collisions of the dissociation products H and NH_2 with the solvent molecules.

Kuhn [100] states that when ultraviolet rays of wave-lengths 2025 to 2140A fall on the compound $2AgCl \cdot 3NH_3$, the ammonia is decomposed.

The irradiation of solutions of alkali metals in liquid ammonia causes a reaction producing the amide ion and hydrogen.[101] The quantum efficiency is a function of both the metal concentration and the wave-length. There is a definite long wave-length threshold at about 2600A and a maximum quantum efficiency at about 2300A. The absorption is similar to that of liquid ammonia. In solutions of the alkali metals, the metal is almost completely dissociated into positive ions and solvated electrons. If the electron collides with the amide radical (produced by photodissociation) before the latter recombines with the hydrogen atom, an amide ion results and the hydrogen then has a greater opportunity to combine with another hydrogen atom. Since the probability that an amide radical will collide with electrons increases with the concentration of the latter, the quantum efficiency should be expected to increase regularly with the concentration, starting at zero and approaching unity asymptotically. This was found to be the case. Since the positive ion plays no essential part in the process, the quantum efficiency should be independent of the nature of the metal. This was true except for deviations encountered with caesium.

The amides of sodium and potassium show very strong continuous absorption throughout the ultraviolet with a maximum near the long wave-length thresholds of 3800-3900A for sodium, and 3950-4150A for potassium, amide. The absorption of light by the electron-ammonia complex, being photochemically inactive, lowers

[95] Mack, E. L., *J. Phys. Chem.*, **21**, 238 (1917).
[96] v. Wartenberg, H., and Klinkott, G., *Z. anorg. allgem. Chem.*, **193**, 409 (1930). See also Glissman, A., and Schumacher, H. J., *Z. physik. Chem.*, **B24**, 328 (1934).
[97] Palmer, F., Jr., *J. Chem. Physics*, **2**, 296 (1934).
[98] Briot, A., and Vodar, B., *Compt. rend.*, **201**, 500 (1935).
[99] Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **55**, 1754 (1933).
[100] Kuhn, W., *Compt. rend.*, **177**, 956 (1923); *Chem. Abs.*, **18**, 789 (1924); *J. chim. Phys.*, **23**, 521 (1926).
[101] Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **55**, 1754 (1933).

the quantum efficiency and accounts for the final yield being less than unity. This work gave a direct method of detecting the NH_2 radical as one of the products of the photodissociation of ammonia. From thermal considerations and the absorption of the metal amides, it appeared that sodium amide is optically dissociated into a normal state sodium atom and a normal state amide radical and is, therefore, ionically bound.

Fearon and M'Kenna[102] state that urea is produced by exposing ammonium carbonate to rays of wave-lengths 2000 to 2500A. The yield is thought to be increased in the presence of malachite green.

In the presence of oxygen or air, solutions of ammonia are oxidized to nitrites when exposed at 35° to 50°C. for three to nine hours to the radiations of a mercury arc.[103] Nitrates were not formed. Ammonium salts were also oxidized to nitrites, the reaction being slower in the case of the sulfate and chloride than in that of the carbonate. Corbet[104] finds hyponitrous acid to be formed as an intermediary product. Gion[105] claimed to have observed the formation of some nitrate in ammonia solutions exposed in quartz vessels to the radiations of a mercury arc. The oxidation proceeded faster at lower temperatures. He claimed also that if only the oxygen in contact with the ammonia solutions and not the solution itself, were irradiated there was oxidation by the ozone formed in the gas. The reaction was said to be sensitized by zinc or titanium oxides.

According to Baur and Renz,[106] ammonia is oxidized to nitrate, and oxalic acid to carbon dioxide on illumination when these substances are adsorbed on thallous chloride. The latter is itself converted to the photochloride.

The acceleration of the photochemical oxidation of ammonia by natural or artificial humus substances[107] or by various catalysts, such as titanium dioxide, alumina or zinc oxide present in soil, has been the subject of many observations, particularly by Indian chemists.[108] Most of these workers believe that ammonium salts are converted through nitrites to nitrates by sunlight in soils under the influence of sensitizers, but some also believe that various organic nitrogen compounds, including urea, amino-acids and uric acid, may similarly yield nitrites and nitrates.

Other workers tend to minimize the importance of photochemical processes in the soil. Fraps and Sterges[109] found that in a large group of samples with different ammonium salts, on the average 5 per cent of the ammonia was oxidized in the sunlight and 41 per cent in the dark. In all cases with corresponding bacterial cultures, those in the dark were oxidized more completely than those in the light. In sterile soils there was no evidence of nitrification. Nitrites in small amounts were found in cultures exposed to light, but little or none in those kept in

[102] Fearon, W. R., and M'Kenna, C. B., *Biochem. J.*, **21**, 1087 (1927).

[103] Kuhn, W., *Compt. rend.*, **152**, 522 (1911).

[104] Corbet, A. S., *Biochem, J.*, **28**, 1575 (1934); **29**, 1086 (1935); Gion, L., *Compt. rend.*, **196**, 344 (1933).

[105] Gion, L., *Compt. rend.*, **195**, 421 (1932).

[106] Baur, E., and Renz, C., *Helv. Chim. Acta*, **15**, 1085 (1932).

[107] Zolcinski, J., *Rocz. Nauk Rolniczych*, **10**, 311 (1923); *Chem. Zentr.*, **96**, I, 1123 (1925).

[108] Dhar, N. R., Bhattacharya, A. K., and Biswas, N. N., *Soil Sci.*, **35**, 281 (1933); Rao, G. G., *Soil Sci.*, **38**, 143 (1934); Dhar, N. R., and Tandon, S. P., *J. Indian Chem. Soc.*, **13**, 180 (1936); *Brit. Chem. Abs.*, **A**, 808 (1936); Sarkaria, A. R., and Fazal-Ud-Din, *Indian J. Agr. Sci.*, **3**, 1057 (1933); **5**, 195 (1935); Desai, S. V., and Fazal-Ud-Din, *Ibid.*, **6**, 777, 985 (1936); Dhar, N. R., and Mukerji, S. K., *J. Indian Chem. Soc.*, **12**, 756 (1936); **13**, 23, 535 (1936); Dhar, N. R., Tandon, S. P., and Mukerji, S. K., *Ibid.*, **12**, 67 (1935); Osugi, S., and Aoki, M., *J. Sci. Soil Manure (Japan)*, **10**, 11 (1936); *Chem. Abs.*, **30**, 3029 (1936). Dhar has summarized his work on the influence of light on nitrogen fixation in soils in *Proc. Natl. Acad. Sci. India*, **6**, Business matters, 3, 289 (1936); *Chem. Abs.*, **31**, 6392, 6393 (1937); see also Dhar, N. R., Mukerji, S. K., Seshacharyulu, E. V., and Tandon, S. P., *Proc. Natl. Inst. Sci. India*, **3**, 75 (1937); *Chem. Abs.*, **32**, 1840 (1938).

[109] Fraps, G. S., and Sterges, A. J., *Soil Science*, **39**, 85 (1935); *Chem. Abs.*, **29**, 4867 (1935).

darkness. This was taken to indicate that the nitric organisms are less resistant to light than are the nitrous organisms. A few non-sterile cultures of soil treated with ammonium salts and exposed to sunlight contained slightly more nitrate and nitrite than did the corresponding soils kept in darkness. These small increases were, however, attributed to differences in bacterial activity rather than to photonitrification. These authors did not regard their work as eliminating the possibility of photonitrification, but thought that photonitrification has a relatively slight effect upon soil processes.[110]

Nitrites. Sodium nitrite absorbs between 3000 and 4000A.[111] In 2-per cent aqueous solution in a glass cell, the nitrite almost completely absorbs the 3660A line. Although Berthelot and Gaudechon[112] had claimed nitrogen to be evolved as a result of the insolation of ammonium nitrite, Holmes[113] was unable to detect any loss of nitrite from a 2.5*N* solution of ammonium nitrite exposed in a quartz vessel for six hours to a 110-volt quartz mercury arc at a distance of 8-16 cm.

Nitrous acid can, however, be decomposed. Mukerji and Dhar[114] found the velocity coefficients in both the light and dark reactions

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

to increase slowly with increasing concentrations of nitrous acid. The velocity was markedly accelerated by light, especially when closed vessels were used. Also, the velocity is proportional to the cube root of the light intensity, according to Murty and Dhar,[115] who employed the wave-lengths 4725, 5650, 7304 and 8500A. The temperature coefficient is less than unity and the Einstein law does not apply.

The influence of light upon the reaction between iodine and potassium nitrite has been studied by Berthoud and Berger.[116] The overall reaction is $KNO_2 + I_2 + H_2O \longrightarrow KNO_3 + 2HI$. In blue light the temperature coefficient is 1.30 between 35° and 45°C. The quantum yield is low, 22 quanta being required to cause one molecule of iodine to react in a solution containing 0.1 mole of potassium iodide and 1 mole of nitrite.[117] In the case of sodium nitrite, the quantum yield varies from 0.005 to 0.1 in phosphate buffers. The yield is independent of the pH, initial concentration of iodine, and rate of absorption of energy (4360A, 5460A, 5790A), but depends on the wave-length, temperature and concentrations of nitrite and iodine atoms. Also, the quantum yield decreases with increasing ionic strength.[118]

Nitrates. The absorption of light by the nitrate ion has been much studied.[119] It consists of two broad bands with maxima at 3100 and at about

[110] See also Corbet, A. S., *Trans. Third Intern. Congress Soil Sci., Oxford*, **1**, 133 (1935); Waksman, S. A., Madhok, M. R., and Hollaender, A., *Soil Sci.*, **44**, 441 (1937); *Chem. Abs.*, **32**, 1376, 2670 (1938); Nath, B. V., *Sci. Repts. Imp. Agr. Research Inst. New Delhi*, 98 (1937); *Chem. Abs.*, **32**, 4265 (1938); Joshi, N. V., and Biswas, S. C., *Trans. Third Intern. Congr. Soil Sci., Oxford*, **3**, 104 (1935); *Chem. Abs.*, **32**, 5567 (1938).

[111] Weber, K., *Chem. Ztg.*, **56**, 642 (1932); *Phot. Korr.*, **66**, 317 (1930).

[112] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 522 (1911).

[113] Holmes, M., *J. Chem. Soc.*, 1898 **(1926)**.

[114] Mukerji, B. K., and Dhar, N. R., *Z. Elektrochem.*, **31**, 255 (1925).

[115] Murty, K. S., and Dhar, N. R., *J. Indian Chem. Soc.*, **7**, 985 (1930); *Chem. Abs.*, **25**, 2921 (1931).

[116] Berthoud, A., and Berger, W. E., *Helv. Chim. Acta*, **11**, 354 (1928); *J. chim. phys.*, **25**, 542 (1928).

[117] It was pointed out that previous work by Mukerji, B., and Dhar, N., [*Z. Elektrochem.*, **31**, 621 (1925)] was in error because of the use of an unsuitable analytical method.

[118] Durrant, G. G., Griffith, R. O., and McKeown, A., *Trans. Faraday Soc.*, **34**, 389 (1938).

[119] Scheibe, G., *Ber.*, **59**, 2616 (1926); Morton, R. A., and Riding, R. W., *Proc. Roy. Soc.*, **113A**, 717 (1927); von Halban, H., and Eisenbrand, J., *Z. wiss. Phot.*, **25**, 149 (1928); Ley, H., and Volbert, F., *Ibid.*, **23**, 41 (1925); *Z. physik. Chem.*, **130**, 308 (1927); Eeckhout, J., *Naturw. Tijdschr.*, **17**, 72 (1935).

2060A, separated by a minimum at about 2600A. Krishnan and Guha [120] attribute the longer wave-length maximum to dissociation into nitrite ion and an oxygen atom and the second band to a similar dissociation producing an excited oxygen atom. Morton and Riding found that at concentrations greater than 0.025*N*, Beer's law fails, the band shifting in the direction of higher extinction coefficients, due to a superposed band which alone is present when very concentrated solutions are employed. Hantzsch and others have found that in concentrated nitric acid or in dilute solutions of nitric acid or alkyl nitrates in ether the band at 3100A is replaced by one at 2700A. This has been said to represent the absorption of a "pseudo-acid" form of nitric acid.[121]

Baudisch and Mayer [122] observed that when aqueous solutions of potassium nitrate are exposed in a flat dish to the rays of a mercury lamp, oxygen is liberated, a blue coloration from starch and potassium iodide being produced in five to ten seconds. The interposition of a glass plate delays the change for twenty minutes. Warburg [123] made the first liquid-phase quantum yield determinations of the change of nitrates to nitrites. Since he observed that the photolysis proceeds much more rapidly in slightly alkaline than in neutral or in acid solutions, he employed solutions 0.00033 molar in sodium hydroxide. (This effect of pH was less apparent when more concentrated nitrate solutions were used.) In 0.33 molar potassium nitrate solutions the values of the quantum yield were 0.25 at 2070A, 0.17 at 2530A and 0.024 at 2820A. That the yields were low he explained by assuming that the efficiency of the dissociation is in some manner affected by the solvent. The fact that the yield decreases with increasing wave-length is readily interpreted by assuming that dissociation by larger quanta endows the dissociation products with sufficient kinetic energy to enable them more effectively to resist the imprisoning effect of surrounding solvent molecules which would tend to lower the quantum yields by inducing a recombination. Warburg also observed that for a given wave-length the quantum yield decreases with the concentration of the nitrate.

Anderson,[124] however, attempted to account for the low yields on the assumption that a reverse reaction may also occur, a "steady state" being reached when only a small portion of the nitrate had been decomposed. He supported this with the statement that the addition of small quantities of potassium nitrite partly or completely inhibited the photolysis of the nitrate. Villars [125] and also Vogels [126] found no evidence for the existence of a "steady state" in this reaction. The decomposition maintains a linear rate for at least 480 minutes. Warburg calculated on the basis of the then available thermochemical data that the energy required to split an oxygen atom from the nitrate ion corresponds to a wave-length between 2800 and 3150A. The observations of Villars and of Warburg (Figure 114) indicate, however, that the drop in quantum yield occurs at a wave-length corresponding to a quantum much larger than that just required to effect the

[120] Krishnan, K. S., and Guha, A. C., *Current Sci.*, **2**, 476 (1934); *Chem. Abs.*, **28**, 6370 (1934); *Proc. Indian Acad. Sci.*, **1A**, 242 (1934); *Chem. Abs.*, **29**, 1326 (1935).

[121] See also Siegler-Soru, E., *Compt. rend.*, **183**, 1038 (1926). For absorption of the crystals, see Rodloff, G., *Z. Physik.*, **91**, 511 (1934).

[122] Baudisch, O., and Mayer, E., *Ber.*, **45**, 1771 (1912); Baudisch, O., and Benford, F., *Naturwiss.*, **24**, 361 (1936).

[123] Warburg, E., *Sitz. Preuss. Akad. Wiss. Math. phys. Klasse*, 1228 (1918); *Chem. Abs.*, **14**, 1930 (1920); *Z. Elektrochem.*, **25**, 334 (1919).

[124] Anderson, W. T., Jr., *J. Am. Chem. Soc.*, **46**, 797 (1924).

[125] Villars, D. S., *J. Am. Chem. Soc.*, **49**, 326 (1927).

[126] Vogels, H., *Bull. sci. acad. roy. Belg.*, **22**, 320 (1936); *Chem. Abs.*, **30**, 6650 (1936); *Brit. Chem. Abs.*, **A**, 687 (1936).

decomposition. The explanation is probably to be found in the detailed mechanism of the recombination processes which occur in aqueous solution. Villars had difficulty in accounting for the fact that measurable quantum yields could be obtained by the use of the wave-length 3350A, which he believed not to possess the requisite energy for dissociation. This difficulty has been removed by a more accurate knowledge of the heat of dissociation of oxygen, which makes the present value of the energy required for the decomposition correspond to about 3500A.[127] Villars also made more precise the data on the effect of pH. In either polychromatic or monochromatic light of 2537A the rates of decomposition increased at pH values slightly above 9 to maxima between 9 and 10, followed by relatively slight decreases at higher pH values. Vogels observed that the pH falls during photolysis, and that the rate may be accelerated by tartrates or, after a delay, by manganous salts.

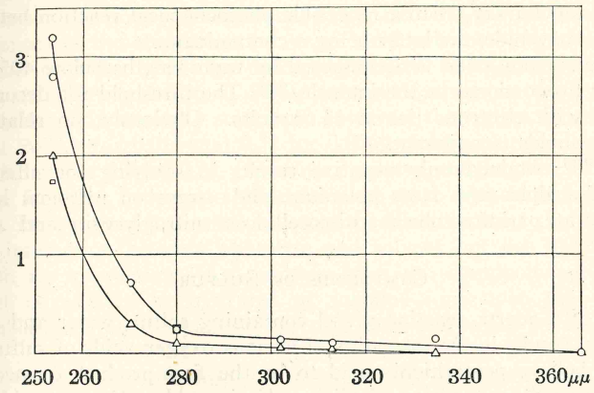


FIGURE 114. Quantum Efficiency of Monochromatic Light Absorbed by M. KNO_3. o = $\phi \times 10$ (buffered, pH 9.9). △ = $\phi \times 10^2$ (unbuffered, pH 5.8). □ = $\phi \times 10$ (Warburg, KNO_3 0.33 M, NaOH 0.0003M) where ϕ = moles transformed per quantum absorbed (Villars, *Journal American Chemical Society*).

Cultrera [128] finds that with mercury lamp irradiation, the reduction of nitrates may proceed to the formation of ammonia.

The decomposition of nitrate crystals appears to be confined to a surface layer not more than 20μ thick. At greater depths, recombination appears to be complete, since the oxygen cannot escape. Polarized rays with vibrations along the normal to the plane of the nitrate ions are much less effective than those with vibrations in the plane of the ions. In crystals, the wave-length threshold is much shorter, 2500A.[129]

Mercury nitrate also undergoes a photochemical change in aqueous solution, the sensitivity of the nitrate being increased by addition of alcohol or glycerol.[130] Fazal-ud-Din [131] has stated that the reduction of solutions of a number of nitrates

[127] Note also Hymas, F. C., *J. Soc. Chem. Ind.*, **50**, 193T (1931).

[128] Cultrera, R., *Gazz. chim. ital.*, **66**, 440 (1936); *Chem. Abs.*, **31**, 3389 (1937); *Ann. staz. sper. agrar. Modena*, **5**, 163, 175 (1936); *Chem. Abs.*, **32**, 3266 (1938).

[129] Krishnan, K. S., and Narayanaswamy, L. K., *Current Sci.*, **3**, 417 (1935); *Brit. Chem. Abs.*, **A**, 682 (1935); *Trans. Faraday Soc.*, **31**, 1411 (1935).

[130] Shljivic, S., and Nicolic, D., *Bull. soc. chim. roy. Yougoslav*, **6**, 159 (1936); *Chem. Abs.*, **30**, 4761 (1936); *cf.* Mudrovcic, M., *Bull. soc. chim. roy. Yougoslav.*, **7**, 41 (1936).

[131] Fazal-ud-Din, *Indian J. Agr. Sci.*, **6**, 844 (1936); *Chem. Abs.*, **30**, 8493 (1936); see also Rao, G. G., and Murty, K. S., *Proc. Natl. Inst. Sci. India*, **3**, 133 (1937); *Chem. Abs.*, **32**, 2028 (1938).

(1 mg. per cc.) can be brought about by sunlight although ultraviolet is more effective. This is in line with the data of Villars. Decomposition is said to be increased by the presence of reduced nickel or carbohydrates, but not to occur in the presence of zinc oxide.

The oxides N_2O_5, TeO_3 and MoO_3 exhibit two regions of continuous absorption separated by a band of transmitted radiation.[132] The first band, in each case, is interpreted as resulting from the separation of an oxygen atom in the ^3P state from the molecule, and the second as resulting from the separation of an oxygen atom in the metastable ^1D state. From the absorption of N_2O_5 the heat of dissociation of oxygen could be calculated to be 128 kcal, not far from the correct value of 117 kcal.

Other Nitrogen Compounds. That commercial sodium cyanide made from calcium cyanamide develops color in light and bleaches in darkness is attributed by Buchanan and Barsky[133] to a reversible photochemical reaction between cyanamide and a ferrocyanide, the latter being a contaminant.

Crystalline sodium azide is decomposed by wave-lengths below 4050A, the rate being directly proportional to the intensity.[134] The threshold for decomposition by bombardment with electrons lies at 11.65 volts. Obviously, no relation between these two thresholds is apparent.

Murarour[135] obtained only negative results in studying the effects of ultraviolet light, the alpha-rays from polonium, and x-rays on nitrogen iodide, picric acid, lead picrate, trinitrotoluene, nitrocellulose, nitroglycerin and *sym.*-diethyldiphenylurea.[136]

Compounds of Sulfur

Exposure of a quartz reaction vessel containing sulfur, water and air to ultraviolet radiation results in the formation of various oxygen acids of sulfur. Dubrisay and Pallu[137] believe pentathionic acid to be the first product formed; this then slowly undergoes decomposition yielding sulfuric acid, sulfurous acid, sulfur and hydrogen sulfide.

The photochemical reaction between yellow arsenic and sulfur dissolved in carbon disulfide results in the formation of insoluble sulfides whose properties differ from those of known sulfides or of a mixture of the elements.[138]

By irradiating mixtures of carbon disulfide and carbon tetrachloride in a Vita-glass screened mercury vapor lamp, Doran and Gillam[139] obtained a polymer of carbon monosulfide as a reddish-brown solid. Nicholes, Simmons and Crockford,[140] state that carbon disulfide is not decomposed by the 3660A line, but that the 2537A line, or a mercury arc in Pyrex leads to the formation of decomposition products including $(CS)_x$, C_3S_2 and a yellowish-brown solid $(C_3S_2)_x$.[141]

Sulfur dichloride absorbs strongly all wave-lengths shorter than 6200A. The

[132] Dutta, A. K., and Gupta, P. K., *Proc. Roy. Soc.*, **139A**, 397 (1933).

[133] Buchanan, G. H., and Barsky, G., *Z. angew. Chem.*, **44**, 383 (1931).

[134] Müller, R. H., and Brous, G. C., *J. Chem. Physics*, **1**, 482 (1933).

[135] Murarour, H., *Bull. soc. Chim.*, **53**, 612 (1933).

[136] Mada, T. [Japanese P. 101,815, July 1, 1933], claims to prepare a nonhygroscopic sodium bicarbonate by raying with ultraviolet for about twenty minutes.

[137] Dubrisay, R., and Pallu, R., *Compt. rend.*, **193**, 339 (1931). See also Calcagni, G., *Gass. chim. ital.*, **65**, 558 (1936); *Chem. Abs.*, **30**, 384 (1936).

[138] Haenny, Ch., *Helv. Chim. Acta*, **13**, 725 (1930); *Chem. Abs.*, **25**, 643 (1931).

[139] Doran, W., and Gillam, A. E., *J. Soc. Chem. Ind.*, **47**, 259T (1928).

[140] Nicholes, P. M., Simmons, N. L., Jr., and Crockford, H. D., *J. Elsiha Mitchell Sci. Soc.*, **52**, 51 (1936); *Chem. Abs.* **30**, 7457 (1936).

[141] For the absorption spectrum of carbon disulfide, see Bruhat, G., and Pauthenier, M., *Compt. rend.*, **181**, 104 (1925); *J. Phys. Radium*, **6**, 287 (1925).

monochloride shows a strong maximum at 2660A.[142] The photochemical reaction between sulfur monochloride and chlorine has an induction period which may be lessened by substituting sunlight for diffused daylight. The rate of reaction is also greater in sunlight. The reaction may be catalyzed by antimony pentachloride.[143] Sulfur dichloride is one of the final products of the dissociation of sulfur monochloride by the action of light, S_3Cl_4 being an intermediate product.[144] When sulfur dichloride is heated or irradiated it undergoes changes in density, the course being that of a first order reaction. The velocity of reversion after irradiation is higher than after displacement by heat, probably because of the formation of a catalyst by the action of light.

Hydrogen Sulfide. Solutions of hydrogen sulfide in water and hexane have, according to Ley and Arends,[145] practically the same absorption curve, the maximum, at 1890A, being attributed to undissociated molecules. Absorption at 2270A in aqueous solutions was attributed to the HS^- ion. Warburg and Rump[146] found differences in the absorption curves in these solvents. Warburg found that in hexane the quantum yield for decomposition of hydrogen sulfide is 0.97 at 2070A, 0.95 at 2220A and 0.96 at 2530A, the concentrations being 0.251, 0.1355 and 0.0452 molar. In aqueous solutions, however, the values were much lower, being 0.43 at 2070A for 0.015 and 0.32 for 0.0369 molar solutions. At 2220A, the yield was 0.32 and at 2530A 0.22. Warburg pointed out that the difference might be due to the fact that hydrogen sulfide does not react with hexane but does react with water. He believed it possible to apply the Einstein law to solutions in which there is no interaction between photolyte and solvent but not to those in which there is such an interaction. An analysis from the standpoint of the influence which might be exerted by hydrated or solvated ions upon the recombination processes subsequent to the primary process does not seem to have been made as yet.

Sulfites. Albu and Goldfinger[147] have studied the absorption of the sulfite ion on the basis of the Franck-Haber theory of the electron-affinity spectrum of ions. Within the range 5000 to 1950A the absorption spectrum depends only upon the pH and concentration of the solutions, and not on their age or method of preparation, provided autoxidation is prevented. The absorption of dissolved undissociated sulfur dioxide can be observed at pH 4 or lower. Absorption begins at 3270A and has a maximum at 2800A. The spectrum of the sulfite ion SO_3'', a structureless electron-affinity spectrum, may be observed in solutions of pH greater than 6. The sulfite ion spectrum has a long wave-length limit of 2660A and corresponds to the process:[148] $SO_3^{--}(H_2O) + h\nu \rightarrow SO_3^- + H + OH^-$. The Franck-Haber theory predicts that the corresponding electron-affinity spectrum of the bisulfite ion should be 1.5 to 2 e-volts to the short wave-length side of that of the sulfite ion. In agreement with this prediction, there was found to be no absorption by the bisulfite ion at wave-lengths greater than 2250A. The long wave-length limits of the absorption by the $S_2O_8^{--}$ and $S_2O_6^{--}$ ions are 2700 and 2600A, respectively. No absorption by the sulfate ion could be detected. Haber and Wansbrough-

[142] Lowry, T. M., and Jessop, G., *J. Chem. Soc.*, 1421 (1929); Lorenz, L., and Samuel, R., *Z. physik. Chem.*, **14B**, 219 (1931).

[143] Bothamley, R. P., *Trans. Faraday Soc.*, **24**, 47 (1928).

[144] Spong, A. H., *J. Chem. Soc.*, 485 (1934).

[145] Ley, H., and Arends, B., *Z. physik. Chem.*, **15B**, 311 (1932).

[146] Warburg, E., and Rump, W., *Z. Physik*, **58**, 291 (1930). Studies in dichloromethane, chloroform and carbon tetrachloride as solvents are due to Avery, W. H., and Forbes, G. S., *J. Am. Chem. Soc.*, **60**, 1005 (1938).

[147] Albu, H. W., and Goldfinger, P., *Z. physik. Chem.*, **16B**, 338 (1932).

[148] See for another interpretation, Farkas, L., and Farkas, A., *Trans. Faraday Soc.*, **34**, 1113 (1938).

Jones [149] have studied the photochemical reaction which (in the absence of oxygen) occurs subsequent to the primary process postulated above. As secondary reactions there might be expected a combination of the hydrogen atoms to molecular hydrogen and a combination of two SO_3^- ions into a dithionate ion $S_2O_6^{--}$. The quantum yields were, however, very small for the formation of dithionate ions, being about 0.07 at pH 9 and decreasing at greater alkalinities. Instead, the majority of the SO_3^- ions formed in the primary process combine with hydrogen atoms to form bisulfite ions.

In the presence of air, ultraviolet (2300-2800A) accelerates the thermal oxidation of sodium sulfite. A 0.2*N* solution of sodium sulfite is completely oxidized in light in about three hours. A particularly interesting feature is the inhibiting effect of small quantities of various substances. According to Mathews and Dewey [150] pyridine strongly inhibited the process when present in the concentration of 5 cc. per liter. Methyl and ethyl acetate had a much weaker effect. Five drops of benzaldehyde per liter strongly inhibited the reaction but the same amount of glycerol produced only a slight effect. Urea had no effect. Hydroquinone and phenol were effective but not as much so as quinine sulfate. Sucrose (0.025*N*) produced less inhibition than did phenol (0.001*N*).[151]

Bäckström [152] reported a series of investigations on the behavior of inhibitors, particularly alcohols, which did much to explain the nature of the photochemical oxidation and of the thermal one as well. It was shown that the photochemical process is a chain reaction, the quantum yields in the absence of inhibitors corresponding to an uptake of about 50,000 molecules of oxygen per quantum absorbed. Since in general, the inhibitors of the photochemical reaction also inhibited the thermal one, it followed that the latter was a chain reaction as well. The role of the inhibitor in both cases consists in the breaking of chains, probably by an induced reaction between the inhibitor and one of the reactants. Attention was devoted to the mechanism of the inhibition and to the length of the chains when broken rather than to the nature of the chains, since the work was done before the theory of the electron affinity spectrum had been developed.

The rates of the light and dark reactions could be represented by the formulas:

$$V_{\text{light}} = k_3 v_{\text{dark}} \text{ and } V_{\text{dark}} = \frac{k_1}{kC + k_2}$$

in which k_1, k_2 and k_3 are constants applicable to all alcohols as inhibitors, k is a specific constant for each inhibitor and C is the concentration of the inhibitor. The form of the equations suggested that the presence of the alcohols did not affect the rate of starting the chains so that the inhibitors function solely by breaking the chains. The constant k_2 indicates that some chains may be broken by processes independent of the presence of added inhibitor. In the case of the thermal reaction it was shown that the alcohols were oxidized in breaking the chains. The amount of oxidation of alcohols could be determined by colorimetric measurements of the aldehydes and ketones produced. At low inhibitor concentrations the amount of alcohol oxidized increases with increasing alcohol concentration. At high inhibitor concentrations the amount of alcohol oxidized per unit time is constant, and independent of concentration, in either the thermal or photochemical oxidation. Over a considerable range of high inhibitor (isopropyl alcohol) concentrations, the product of the rate of sulfite oxidation and inhibitor remained constant, and the ratio between this product and the amount of acetone formed was the same, 74 to 77, in the thermal and in the photochemical oxidations. From this it followed that in a solution of a given composition the chain length is the same whether the chains are formed thermally or photochemically.

A solution 0.1*M* with respect to benzyl alcohol gave a quantum yield of 64 molecules of oxygen or 128 of sulfite reacting per quantum. From the amount of acetone formed it was determined that the number of molecules of sulfite oxidized for each molecule of alcohol oxidized was 58, of the same order of magnitude. This indicates that in the process of breaking a reaction chain, 2.2 molecules of the alcohol are oxidized. In other words, the induced oxidation of benzyl alcohol has a quantum yield of 2.2. It was later found by Bäckström [153] that light intensity enters into the rate equation as approximately the half power, both in the numerator and in an additional term in the denominator. The reaction had a pH dependence which suggested that both sulfite and bisulfite ions must be concerned in the mechanism. When oxidation occurs, the primary SO_3^- probably forms an intermediary SO_5^- ion which dehydrogenates the bisulfite ion, present at the effective pH, producing a sulfate ion and reforming the SO_3^- ion which can again be oxidized. The inhibiting action of the alcohol is due to its induced oxidation, probably by the assumed SO_5^- ion.

Allmand and Maddison [154] believed that light of ordinary wave-lengths has no effect on the rate of oxidation of sodium sulfite in solution. Titoff [155] found that copper sulfate is without effect upon the ultraviolet reaction, but catalyzes the reaction in ordinary light. Franck and Haber [156] postulate that the effect of the copper ion is to start the thermal reaction by forming the ion SO_3^- the same ion as that later found by Bäckström to be the primary product in the photoreaction.[157]

Persulfates. That aqueous solutions of potassium persulfate are light-sensitive was demonstrated by Dhar [158] and Elbs and Neher.[159]

In a series of investigations, Morgan and Crist [160] found that the reaction could be expressed by the equation:

$$K_2S_2O_8 + H_2O \longrightarrow 2KHSO_4 + 1/2O_2$$

In very dilute solutions, the order of reaction was unimolecular, as is the thermal reaction which occurs at higher temperatures. In concentrated solutions which absorbed all the light, the reaction was of zero order. Increasing the oxygen

[149] Haber, F., and Wansbrough-Jones, O. H., *Z. physik. Chem.*, **18B**, 103 (1932).

[150] Mathews, J. H., and Dewey, L. H., *Eighth Intern. Congr. Appl. Chem., Sect. IX, Orig. Comm.*, **20**, 247 (1912); *J. Am. Chem. Soc.*, **39**, 635 (1917).

[151] Mathews, J. H., and Mason, R. B., *J. Phys. Chem.*, **30**, 414 (1926) later erroneously stated the phenols to act as positive catalysts.

[152] Bäckström, H., *J. Am. Chem. Soc.*, **49**, 1460 (1927); *Medd. Kgl. Vetenskapsakad. Nobelinst.*, **6**, No. 16 (1927); Bäckström, H., and Alyea, H. N., *J. Am. Chem Soc.*, **51**, 90 (1929).

[153] Bäckström, H., *Z. physik. Chem.*, **25B**, 122 (1934).

[154] Allmand, A. J., and Maddison, R. E. W., *J. Chem. Soc.*, 650 (1927).

[155] Titoff, A., *Z. physik. Chem.*, **45**, 641 (1903).

[156] Franck, J., and Haber, F., *Sitzber. Preuss. Akad. Wiss.*, 250 (1931); see also Albu, H. W., and von Schweinitz, H. D., *Ber.*, **65B**, 729 (1932).

[157] There have from time to time been efforts to employ ultraviolet light in the preparation of sulfuric acid. Kühne, H., French P. 393,461, 1908; *J. Soc. Chem. Ind.*, **28**, 90 (1909); British P. 17,520, 1908; *J. Soc. Chem. Ind.*, **28**, 982 (1909). German P. 203,541; Chmura, T., *Chem. Age*, **13**, 327,307 (1925); British P. 237,257; de Sotto, G. E., British P. 265,857, July 20, 1926. No practical applications have been made.

[158] Dhar, N. R., *Proc. Akad. Vetensk.*, **23**, 308 (1920).

[159] Elbs, K., and Neher, P., *Chem. Z.*, **45**, 1113 (1921).

[160] Morgan, J. L. R., and Crist, R. H., *J. Am. Chem. Soc.*, **49**, 16, 338, 960 (1927).

concentration did not reverse the reaction. Hydrogen and nitrogen appeared to exhibit an accelerating effect. Potassium persulfate absorbs only wave-lengths shorter than about 2500A in a 0.01*M* solution and 3000A in a 0.1*M* solution. The upper limit of the radiations effective in producing the decomposition was probably at about 2900A and the maximum sensitivity at about 2300A. The reaction was proportional to the light intensity, and the temperature coefficient was 1.18, compared with about 3 for the thermal reaction. The rate of reaction was retarded by the addition of potassium hydroxide, potassium sulfate or sulfuric acid. The retardation was not due to internal filtering, was hyperbolic and seemed to be of the same general nature in the presence of various added electrolytes. The quantum efficiency was unity in 0.05 molar neutral or alkaline solutions, the wave-lengths used being 2540, 2650 and 3020A.[161] In acid solutions the values of the quantum yield are somewhat reduced. Solid potassium persulfate is also decomposed by ultraviolet light.

Marmier[162] has reported that decomposition of aqueous solutions of sodium thiosulfate results in the formation of sulfur and hydrosulfite. The latter was rapidly decomposed by ultraviolet and after an exposure of 75 minutes under the conditions of observation no traces remained.

Ammonium Thiocyanate. Holmes[163] observed that freshly prepared concentrated solutions of ammonium thiocyanate exposed to ultraviolet light in glass containers evolved a gas and developed a reddish color which soon faded. In quartz containers, sulfur separated from the solution. Werner and Bailey[164] suggested that the photoreaction involved only the production of ammonia and thiocyanic acid, the color being due to traces of iron as impurity. This theory was corroborated by Patten and Smith.[165] According to these investigators, light accelerates oxidation of the iron so that the latter can react with the thiocyanate. Wave-lengths less than 5400A produced the coloration, those between 4000 and 4300A being the most effective. Sharma[166] considered the color to be due to a loose additive complex of ferrous thiocyanate with oxygen.

Shorter wave-lengths (3000-1850A) can decompose thiocyanates of ammonium, sodium or potassium with liberation of sulfur, according to Jablczynski and Jablczynska.[167] The reaction is believed to be reversed in the dark.

The velocity of solution of amorphous selenium is increased by light but that of monoclinic selenium is not affected.[168]

Arsenic and Antimony Compounds

An account of the investigations on the source of the glow of arsenic at high temperatures is beyond the scope of this work.[169] Lead arsenite is photosensitive. When dried in an air-bath in the dark, it remains white, but when exposed to light it turns brown. Mixed with gelatin and applied to paper and dried in the dark, it can be used in photography, developing warm sepia tones when exposed under a negative. Not all samples of lead arsenite possess this property. No other metallic arsenites are light-sensitive.[170]

Detailed determinations have been made by Weigel[171] of the absorption of light and the electrical conductivity of realgar when the crystal is exposed to light of various wave-lengths. Fragments of realgar exposed to direct sunlight for 112 hours behind sheets of glass of various colors showed the greatest change with a green glass of maximum transparency near 520μ.

Solutions of antimony oxide in hydrochloric or tartaric acids and of antimony trichloride in saturated sodium chloride solution in ordinary glass vessels are photochemically oxidizable by sunlight.[172] Light of shorter wave-length is required in the case of solutions of antimony trioxide or of tartar emetic in sulfuric acid, or of antimony trichloride in carbon tetrachloride and in saturated calcium chloride solution. The amount of oxidation depends on the kind of solution, wave-length and intensity of the radiation and concentrations of antimony and of oxygen.

In carbon disulfide, white phosphorus is converted by light into red phosphorus, a dissociation and recombination being involved.[173]

When boron hydride, B_4H_{10}, is kept over mercury at room temperature, it slowly undergoes decomposition with the formation of the hydride, B_2H_6. The decomposition is accelerated greatly by ultraviolet rays, but not by sunlight.[174]

Metals and Salts

Under the influence of light, copper combines with chlorine[175] but not with bromine or iodine; with oxygen, but not with sulfur; with water, but not with hydrogen sulfide; with ammonia, but not with phosphine or arsine. Aqueous solutions of the chlorides or sulfates of gold, silver, uranium, copper, nickel, chromium and cobalt were reported by Berthelot and Gaudechon[176] to be unaffected by ultraviolet radiation. The sulfates of nickel and cobalt gave a slight brown precipitate, attributed to the presence of traces of iron. Solutions of ferrous sulfate gave a precipitate of the basic salt. Pure ferric sulfate did not give a precipitate but in the presence of nickel or cobalt sulfate precipitated the basic salt. Urbain and Scal[177] stated that the pasasge of rays (from an arc) through tetrachlorides of titanium, tin, or carbon, caused a marked decomposition, chlorine being liberated.

A method of depositing metals has been advocated by Jacquier.[178] The process comprises precipitating metals from solutions of their salts by treatment with ultraviolet rays in the presence of aluminum. Mercury vapor lamps are suspended between aluminum plates in the tank containing the solution to be treated.

Light is believed to facilitate the reduction of some metallic oxides. Actinic rays are said to promote the interaction of oxygenated compounds (*e.g.*, calcium phosphate), barytes or bauxite with chlorine in the presence of a reducing

[161] Crist, R. H., *J. Am. Chem. Soc.*, **54**, 3939 (1932).
[162] Marmier, L., *Compt. rend.*, **154**, 32 (1912).
[163] Holmes, M., *J. Chem. Soc.*, 1690 (1926).
[164] Werner, E. A., and Bailey, K. C., *J. Chem. Soc.* 2970 (1926); more complicated theories of the origin of the color were suggested by Holmes, M., and by Bhatnagar, S., Dunnicliffe, H., and Ali, M., *J. Indian Chem. Soc.*, **4**, 229 (1927).
[165] Patten, C. G., and Smith, H. D., *Trans. Roy. Soc. Canada*, **22**, 221 (1928).
[166] Sharma, B. S., *J. Chem. Soc.*, 308 (1930); see also Rao, S. V., *J. Chem. Soc.*, 880 (1934).
[167] Jablczynski, K., and Jablczynska, H., *Roczniki Chem.*, **10**, 579 (1930); *Chem. Abs.*, **25**, 877 (1931).
[168] Shidei, J., Hashizuma, S., and Kitahara, S., *Bull. Chem. Soc. Japan*, **10**, 374 (1935); *Brit. Chem. Abs.*, **A**, 1331 (1935); Sterzel, S. E., and Afzelius, I., *Svensk Kem. Tidskr.*, **49**, 281 (1937); *Brit. Chem. Abs.*, A (I), 90 (1938).
[169] Emeléus, H. J., *J. Chem. Soc.*, 783 (1927). For phosphorus, Emeléus, H. J., *Nature*, **115**, 460 (1925); *J. Chem. Soc.*, 1336 (1926); Emeléus, H. J., and Purcell, R. H., *J. Chem. Soc.*, 788 (1927); Petrikaln, A., *Naturwiss.*, **16**, 205 (1928); Miller, C. C., *J. Chem. Soc.*, 1823, 1829 (1929).

[170] Reissaus, G. C., *Z. angew. Chem.*, **44**, 959 (1931).
[171] Weigel, O., *Tech. Min. Petr. Mitt.*, **38**, 288 (1925); *Chem. Abs.*, **20**, 3268 (1926).
[172] Brüll, W., with Schlägel, H., *Z. anorg. Chem.*, **217**, 401 (1934).
[173] Rathenau, G., *Physica*, **4**, 503 (1937); *Chem. Abs.*, **31**, 6560 (1937).
[174] Stock, A., and Friederici, K., *Ber.*, **46**, 1959 (1913).
[175] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **157**, 129 (1915).
[176] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 376 (1911).
[177] Urbain, E., and Scal, C., *Compt. rend.*, **168**, 887 (1919).
[178] Jacquier, G., British P. 17,790, Aug. 2, 1913.

agent such as carbon. At temperatures between 200° and 1000°C., inorganic halides are said to be secured.[179]

The yellow amorphous modification of indium oxide is sensitive to light when in the presence of some reducing agents as benzaldehyde. The color of the oxide changes from gray to dark gray or black. Also, some reduction products are formed. Selenium oxide is not sensitive under the same conditions.[180]

Krauss and Gerlach[181] found that the preparation of iridium halides by the action of the halogens upon iridium or its hydroxide could be hastened by the action of light.

Hibben[182] observed that some large crystals of magnesia became tinted a deep purple on exposure to the 2537A line. On removal from the light, spontaneous decolorization occurred in several weeks at 25°C., or in three minutes at 1000°C. It was accompanied by emission of light throughout the visible spectrum. The first effect was ascribed to a type of electron migration, and the later effects to a recombination. It may be related to the presence of impurities since not all crystals behave alike. The 4358A line decolorized the purple crystals in thirty minutes.[183]

Light from a carbon arc accelerates the rate of evolution of hydrogen from dilute sodium and potassium amalgams in water.[184]

Iron Salts. That ferrous hydroxide and sulfate are more rapidly oxidized in light than in darkness was first made known by Chastaing.[185] The ferrous ion when irradiated with wave-lengths shorter than 2900A, is oxidized to ferric ion and hydrogen is evolved.

$$Fe^{++} + HOH + h\nu \longrightarrow Fe^{+++} + H + OH^-$$

The quantum yield in aqueous solution is 0.05. The primary process is followed by a combination of two hydrogen atoms, which occurs in competition with the reverse reaction. The activation energy of the latter is 7 kcal.[186]

The color of hydrochloric acid solutions of ferric chloride increases on exposure to sunlight or other sources of intense light.[187] On removal from the light, the solutions slowly return to their original condition. Increased light absorption also results from heating a solution of ferric chloride. A crystal of ferric chloride shows, in addition to general absorption starting at 5000A, a sharp band at 6200A, from 50 to 100A in width.[188]

In alcoholic solution, ferric chloride is readily bleached in light by reduction to the ferrous salt, a reaction discovered by Bestucheff in 1725.[189] The reaction is best conducted in the presence of organic substances, either as solvent or added to the solution, or bound in complex form to the iron, since these organic compounds can be oxidized by or react with the chlorine liberated in the photochemical decomposition. A wide variety of organic reducing agents have been studied,

[179] British P. 302,927, Dec. 22, 1927, to Naamlooze Vennootschap Elektrochemische Industrie; *Chem. Abs.*, **23**, 4304 (1929).

[180] Renz, C., *Helv. Chim. Acta*, **15**, 839 (1932); *Chem. Abs.*, **26**, 4754 (1932).

[181] Krauss, F., and Gerlach, H., *Z. anorg. allgem. Chem.*, **147**, 265 (1925).

[182] Hibben, J. H., *Phys. Rev.*, **51**, 530 (1937).

[183] For effects of visible light and x-rays on lead oxides, see Hoffmann, J., *Z. anorg. Chem.*, **228**, 160 (1936).

[184] Bhatnagar, S. S., Prasad, M., and Mukerji, D. M., *Quart. J. Indian Chem. Soc.*, **1**, 263 (1925); *Chem. Abs.*, **19**, 3429 (1925).

[185] Chastaing, P., *Ann. Chem.*, **10**, 145 (1877).

[186] Potterill, R. H., Walker, O. J., and Weiss, J., *Proc. Roy. Soc.*, **A156**, 561 (1936).

[187] Ritchie, K. S., *J. Phys. Chem.*, **32**, 1269 (1928).

[188] Rawlins, F., and Snow, C. P., *Z. Krist.*, **83**, 41 (1932).

[189] Plotnikow, J., "Algemeine Photochemie," p. 410. Berlin, de Gruyter, 1936.

including paper, glycerol, and many acids. It was as a result of the study of this reaction that Grotthuss evolved the law which bears his name.[190] Winther[191] found that aqueous solutions of ferric chloride, when free from organic matter, undergo only a very slight reaction. Puxeddo[192] reported that the reaction in absolute ether follows a monomolecular course. At the end of reaction, the ether was partially chlorinated.

Prasad and Sohoni[193] studied the influence of temperature, light intensity, water and neutral salts on the decomposition of ferric chloride in alcoholic solution. The temperature coefficient is 1.0 to 1.15. In anhydrous solution a steady state is apparently reached, the reaction being reversible. Small amounts of water increase the initial rate of the reaction but seem to decrease the total amount of reduction. Minute quantities of the chlorides of magnesium or the alkalies are strongly inhibiting. Variations of light intensity have a more pronounced influence on the rate of the reduction in dilute solutions than in more concentrated ones. The quantum yield varies from 0.6 to 4 in various alcohols, including methyl, ethyl, propyl and butyl.[194] The quantum yield increases with the concentration of the ferric chloride, the frequency of the light and the temperature. These workers find the products to be ferrous chloride and chlorine, no side reactions occurring within the first two hours. In later work, it was observed that in dilute solutions, two reactions may take place, each of zero order.[195] The initial velocity of the reduction in dilute solutions is proportional to a power of the concentration, which depends on the nature of the solvent. In concentrated solutions, however, the initial velocity is independent of the concentration of the ferric chloride. It was believed unlikely that the primary process involved a photodissociation.[196] There may be either an activation of ferric ions which then react with the alcohols, or an activation of a molecule of ferric chloride, which then reacts with a second molecule to yield ferrous chloride and chlorine, the latter attacking the alcohols. Either mechanism would give a quantum yield of two.

In studying the influence of light upon the decomposition of ferric iron preparations containing citric acid, a decomposition which sometimes causes the stoppers to be blown from bottles by the accumulation of carbon dioxide, Fry and Gerwe[197] reviewed the work on the reduction of ferric salts by organic acids in light. Eder[198] and de Vries[199] found ordinary light to effect the reduction of ferric salts in the presence of oxalic, citric and malic acids. A small amount of ferric chloride oxidized a great excess of acid. Neuberg[200] made an extensive study of the action of both sunlight and ultraviolet light upon sixty substances in the presence of ferric salts and uranic salts. Fry and Gerwe found that three moles of carbon dioxide were produced for each molecule of ferric sulfate reduced. No

[190] Ross, W. H., *J. Am. Chem. Soc.*, **28**, 790 (1906); Schneider, M., *Z. physik. chem. Unterricht.*, **39**, 271 (1927); Benrath, A., *Z. physik. Chem.*, **74**, 115 (1910); Ghosh, J. C., and Mitra, B. N., *J. Indian Chem. Soc.*, **5**, 191 (1928); *Chem. Abs.*, **23**, 21 (1929).

[191] Winther, C., *Z. Elektrochem.*, **18**, 138 (1912); *Z. wiss. Phot.*, **11**, 60 (1912); **9**, 205 (1910).

[192] Puxeddu, E., *Gazz. chim. ital.*, **50**, 154 (1920); **52**, 229 (1922).

[193] Prasad, M., and Sohoni, N. V., *J. Indian Chem. Soc.*, **8**, 489 (1931); *Chem. Abs.*, **26**, 378 (1932).

[194] Prasad, M., and Limaye, P. S., *J. Indian Chem. Soc.*, **10**, 91, 101 (1933); *Chem. Abs.*, **27**, 3882 (1933).

[195] Prasad, M., and Mohile, B. V., *Proc. Natl. Acad. Sci. India*, **6**, 261 (1936); *Chem. Abs.*, **31**, 1298 (1937).

[196] Prasad, M., Mohile, B. V., and Nigudkar, K. D., *J. Univ. Bombay*, **5**, Pt. 2, 142 (1936); *Chem. Abs.*, **31**, 3790 (1937).

[197] Fry, H. S., and Gerwe, E. G., *Ind. Eng. Chem.*, **20**, 1392 (1928).

[198] Eder, J. M., *Monatsh.*, **1**, 755 (1880); *Ber.*, **14**, 1183 (1881).

[199] deVries, H., *Rec. trav. Chim.*, **3**, 365 (1884); *Chem. Zentr.*, **56**, 219 (1885).

[200] Neuberg, C., *Biochem. Z.*, **44**, 495 (1912).

carbon monoxide formed. They proposed a mechanism in which the citric acid is converted into hydrogen, carbon dioxide and acetone-dicarboxylic acid. The latter immediately decomposed to yield a second molecule of carbon dioxide and acetoacetic acid, which in turn, yielded a third molecule of carbon dioxide and acetone. The ferric sulfate was believed to aid the oxidation of the hydrogen formed in the first reaction. The summation of the reactions gave the stoichiometrical ratio between ferric sulfate reduced and carbon dioxide produced which was found experimentally. It is to be noted that the sequence of events was stated to depend upon an action of the light directly upon the citric acid rather than upon the ferric salt. From the preceding discussion, it is evident, however, that in most cases in which ferric salts are photochemically reduced in the presence of organic matter, the light acts primarily upon the ferric salt. Lal and Ganguli [201] reported that the rate of reduction of ferric salts in the presence of a mercury arc as source was proportional to the light intensity. Reduction was strongly accelerated by traces of thorium, uranium, copper and zirconium salts.[202]

Ferrocyanides and Other Complex Salts. A reversible color change occurs in solutions of potassium ferrocyanide in sealed tubes exposed to light. Only after months is there some precipitation of ferrous hydroxide.[203] Equilibrium conditions for a 0.25-per cent solution of potassium ferrocyanide in water are reached after an exposure of thirty minutes to an arc.[204] With exposures of sixty minutes, the percentage decomposition decreased from 0.23 per cent to 0.10 per cent as the concentration of the salt was decreased from 7.67 to 3.07 gm. per 100 cc. A further decrease in the concentration of the salt to 1.53 gm. per 100 cc. resulted in an increase in the decomposition to 0.40 per cent. Up to a certain amount, the presence of potassium hydroxide aids the decomposition, but larger amounts decrease decomposition to the value found for neutral solutions. Complete reversibility of the reaction was shown after the first exposure to light and darkness, but with successive equal exposures the amount of decomposition increased, and the reversibility of the reaction decreased. Baur [205] found oxygen to accentuate the darkening in color of ferrocyanide solutions on illumination, although darkening occurs also with deaerated freshly prepared solutions. In acid solutions, Prussian blue forms. If the ferrocyanide solution is passed through a column of granulated aluminum, the original yellow color disappears, and the solution ceases to be photochemically sensitive. These facts were interpreted as indicating that the ferrocyanide ion itself is photochemically insensitive, the light reaction being due to the photodecomposition of the ferricyanide ion always present in small quantities.

Baudisch [206] observed that ferrous ions, as well as pentacyanoaquoferrite ions, are produced when solutions of potassium ferrocyanide, neutral or feebly acid with carbonic acid, are exposed to the carbon arc or to direct sunlight in the absence of air. In the presence of air and light, the yellow ferrite ions are immediately oxidized to the dark violet pentacyanoaquoferrate ions, which react with the first named ions to form complex compounds that have a pale yellow color. The

[201] Lal, P., and Ganguli, P. B., *Z. anorg. allgem. Chem.*, **229**, 16 (1936).

[202] See also Burt, J. B., *J. Am. Pharm. Assn.*, **17**, 650 (1928) and Purkayastha, R. M., *J. Indian Chem. Soc.*, **9**, 237 (1932).

[203] Baudisch, O., and Bass, L., *Ber.* **55B**, 2698 (1922); *Chem. Abs.*, **16**, 4137 (1922). For the absorption spectra, see Plotnikow, J., and Karschulin, M., *Z. Elektrochem.*, **33**, 212 (1927); Getman, F., *J. Phys. Chem.*, **32**, 187 (1928); Briggs, S., *J. Chem. Soc.*, **99**, 1019 (1911); **117**, 1026 (1920); *J. Phys. Chem.*, **32**, 1422 (1928).

[204] Rossi, G., and Bocchi, C., *Gazz. chim. ital.*, **55**, 876 (1925).

[205] Baur, E., *Helv. Chim. Acta*, **8**, 403 (1925).

[206] Baudisch, O., *Ber.*, **62B**, 2706 (1929).

presence of sodium azide inhibits the formation of these products, and under these conditions the yellow potassium ferrocyanide is oxidized directly to the dark violet potassium pentacyanoaquoferrate ion. In an air-free system, the iron atom of potassium ferrocyanide is activated by light in consequence of the mobilization of its secondary valences. The original inactive compound is rapidly reformed in the dark. In the presence of air and light, peroxo-compounds possessing unusual oxidizing powers are produced in addition to the usual ferric and ferrous complex ions.

Dickinson and Ravitz [207] state that systems containing the ferro- and ferricyanide ions together with the iodide ion and iodine, are sensitive to light not absorbed by the complex cyanides. When light was directed into such an equilibrium mixture, the concentration of titratable iodine increased. The photochemical reaction was believed to be a reduction of ferricyanide to ferrocyanide by iodide, the absorption being almost entirely by the tri-iodide ion. One molecule of iodine was formed for each quantum absorbed. In discussing the possible mechanism of the reaction, these authors suggested the possibility that an iodine atom might react with an iodide ion to produce the ion I_2^- which might then serve as the reducing agent for the ferricyanide.

It is the opinion of Schwarz and Tede [208] that potassium ferricyanide is not appreciably sensitive to light, decomposition taking place to a very slight extent after intense illumination. The change consists in hydrolysis to aquo-complex salts and ultimately ferric hydroxide, and also in the oxidation of hydrocyanic acid to cyanogen with the production of potassium ferrocyanide. In the case of potassium cobalticyanide, the reaction is

$$K_3Co(CN)_6 + H_2O \longrightarrow K_3Co(CN)_5OH + HCN$$

and

$$K_3Co(CN)_6 + H_2O \longrightarrow KCN + K_2Co(CN)_5H_2O.$$

The corresponding chromium compound behaves similarly to the cobalticyanide, but the manganese compound is rapidly decomposed in the absence of light into manganic hydroxide, hydrocyanic acid and potassium cyanide.[209]

Pavolini [210] observed that when paper is coated with a solution of 5-per cent potassium ferricyanide and 5-per cent ammonium molybdate, a print can be made on exposure to sunlight. The exposed print can be fixed in water acidulated with 1-per cent hydrochloric acid. If, on the other hand, these compounds are added to a gelatin or gum arabic solution, the gelatin is rendered insoluble by the decomposition products formed on exposure to light. This mixture produces the same result as do dichromates.

A weak source of light is capable of increasing by about 10 per cent the rate of oxidation of hydrazine by the ferricyanide ion. The effective rays are those absorbed by the ferricyanide.[211]

An aqueous solution of sodium nitroprusside when exposed to sunlight in an open vessel is decomposed into hydrogen cyanide, sodium nitrite and $Na_2Fe_2(CN)_6$, the latter, in the presence of sodium hydroxide, being converted into Prussian

[207] Dickinson, R. G., and Ravitz, S. F., *J. Am. Chem. Soc.*, **52**, 4770 (1930).

[208] Schwarz, R., and Tede, K., *Ber.*, **60**, 69 (1927).

[209] For observations on sodium nitroferrocyanide, see Justin-Mueller, E., *Bull. soc. chim.*, **2**, 1932 (1935).

[210] Pavolini, T., *Corr. fot.*, **26**, 723 (1929); *Chem. Abs.*, **24**, 2958 (1930).

[211] Gilbert, E. C., *J. Phys. Chem.*, **35**, 3631 (1931).

blue.[212] If the exposure to sunlight takes place in a closed vessel, nitric oxide is evolved.

The precipitates formed on mixing a concentrated aqueous solution of sodium nitroprusside with aqueous solutions of silver nitrate, mercuric nitrate, or ferrous sulfate, suffer change after exposure to sunlight for ten minutes.[213]

Potassium permanganate and potassium dichromate are very stable towards ultraviolet light.[214]

Although the chromates of ammonium, potassium and sodium are unaffected by sunlight in the absence of substances capable of oxidation, in the presence of such substances the photochemical reduction of the chromates and dichromates occurs rapidly under the radiations of an arc light.[215] The reduction results in either a brownish precipitate or a green solution according to the properties of the substance which serves as reducing agent. In some cases there is an evolution of gas, either ammonia, in the case of ammonium chromates, or carbon dioxide. According to Bhattacharya and Dhar,[216] the orders of the reactions between chromic acid and the following acids in sunlight and in darkness are, respectively: citric acid, 2, 2.5; tartaric acid, 2,3; lactic acid, 3, 3. Manganous sulfate accelerates most of the reactions and, except in the case of tartaric acid, reduces the order. With decrease in the order of the reaction, the temperature coefficients of the velocity coefficients usually rise. The temperature coefficient for the photochemical reaction is always greater than unity but less than that of the dark reaction with the same acid. In all cases, several molecules react for each quantum absorbed, the number increasing with increase in the concentration and with the temperature. The rate of reaction with or without manganous sulfate is directly proportional to the intensity of the incident radiation, except in the reactions with citric and tartaric acids in the absence of manganous sulfate, the rates of which are proportional to the square root of the intensity of the radiation.

Forbes and Leighton[217] electrolyzed 0.006 to 0.05*N* chromate solutions in normal and three normal sulfuric acid between platinum electrodes at various current densities, comparing the yields obtained in the light of a 1500-watt quartz mercury arc and in darkness. At an illuminated cathode, a 0.5 per cent greater efficiency was observed. Part or all of the increased efficiency could be attributed to local heating in a thin diffusion layer at the cathode. An absence of any increase in yield in light would be compatible with the existence of light-sensitive chromate if the latter is equally reactive electrochemically before and after photoexcitation. Granting, however, that the slightly greater electrochemical efficiency in light may be due in part to excited chromate, it would be impossible to estimate the quantum yield without making certain assumptions, especially one regarding the life of the excited molecule, upon which would depend its chance of reaching the cathode.

[212] Justin-Mueller, E., *Bull. soc. chem.*, **2**, 1932 (1935).

[213] Leffmann, H., and Pines, C. C., *Bull. Wagner Free Inst.*, **4**, 41 (1929); *Brit. Chem. Abs.*, **A**, 1431 (1929).

[214] Mathews, J. H., and Dewey, L. H., *8th Intern. Congr. Appl. Chem. Sect. IX, Orig. Comm.*, **20**, 247 (1912). For data on the absorption of chromic acid, potassium chromate and dichromate and permanganate solutions, see Viterbi, E., and Krausz, G., *Gazz. chim. ital.*, **57**, 690 (1927); Bhagwat, W. V., and Dhar, N. R., *J. Indian Chem. Soc.*, **7**, 913 (1930); *Chem. Abs.*, **25**, 2053 (1931); Tawde, N. R., *J. Indian Chem. Soc.*, **8**, 499 (1931); *Chem. Abs.*, **26**, 395 (1932); Rao, A. L. S., *Current Sci.*, **6**, 154 (1937); *Brit. Chem. Abs.*, **AI**, 59 (1938); *Proc. Indian Acad. Sci.*, **6A**, 293 (1937).

[215] Plotnikow, J., *Bull. acad. sci. Russ.*, 1093 (**1919**); *Chem. Abs.*, **17**, 2231 (1923).

[216] Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. Chem.*, **169**, 381 (1928); see also Wulff, P., and Ammann, H., *Compt. rend. IX, Congr. int. Phot. Sci. appl.*, 10 pp., 1935; *Brit. Chem. Abs.*, **AI**, 90, 1938; Ammann-Brass, H., *Z. wiss. Phot.*, **36**, 33 (1937); *Brit. Chem. Abs.*, **A**, 255, 1937. For the use of a formic acid-formate buffer in the photoreduction, see Wulff, P., and Ammann, H., *Compt. rend., IX^e int. Photo. sci. appl.*, **1935**; *Chem. Abs.*, **31**, 8381 (1937).

[217] Forbes, G. S., and Leighton, P. A., *J. Phys. Chem.*, **30**, 1628 (1926).

Morton[218] finds that, under suitable conditions, as in the presence of ethyl alcohol, dichromate solutions are affected by light absorbed by the dichromate. With increasing acidity, the oxidizing power of the dichromate solutions in darkness increases so that the apparent action of light decreases.

Reactions between potassium dichromate and gelatin under the influence of light have been studied and have been applied in photography. The photochemical mechanism is not yet understood, and no attempt will be made to review the early work on the nature of the reaction. According to Plotnikow and Karschulin,[219] the reaction begins at 5950A, reaches a maximum at 5000A and then decreases to about 2400A, at least in the case of films sensitized with potassium dichromate and cresyl blue, 2BS. On the other hand, Eder[220] found the action of light on chromated gelatin to begin at 550mμ, to reach a maximum between 470 and 430mμ, and to become very slight beyond 380mμ.[221] Popovitzkiĭ[222] states that from earlier work of Eder, it is known that gelatin so transformed represents a compound with chromium salts, no organic oxidation products entering the composition. Popovitzkiĭ suggested the formula $4Cr_2O_3 \cdot 3CrO$, for the chromium complex, which agreed better with the analytical results than the formulas $Cr_2O_3 \cdot 2CrO_3$ or $Cr_2O_3 \cdot 3CrO_3$ suggested by Eder and Lumière Brothers and Seyewetz. In order to employ the Werner coördination number of six for chromium compounds, the formula given above should be doubled. Two photochemical reactions might be written to account for its formation:

$$16K_2CrO_4 \cdot CrO_3 \longrightarrow 16K_2CrO_4 + 8Cr_2O_3 + 12O_2.$$
$$6K_2CrO_4 \cdot CrO_3 \longrightarrow 6K_2CrO_4 + 6CrO_3.$$

It is presumed that the gelatin having absorbed but not combined with the liberated oxygen can enter into combination with the 8 Cr_2O_3 and 6 CrO_3 with greater ease. Galinsky[223] suggests that the change resembles a protein denaturation, although no change in the Hausmann numbers or in the digestibility was detected.

The decomposition of chromyl chloride by light into CrO_2 and chlorine, from the nature of the absorption spectrum, requires wave-lengths shorter than 4200A.[224]

Tin Compounds. The molecular absorption coefficient of a solution containing 32.7 gm. stannous chloride per liter and 0.811*N* in hydrochloric acid corresponds to complete absorption for wave-lengths shorter than 2850A, partial absorption from 3020 to 3340A and complete transmission of wave-lengths longer than 3650A. Stannous chloride solutions do not follow Beer's law, probably because of the formation of such absorbing complexes as $HSnCl_3$ and H_2SnCl_4 in the presence of increasing amounts of acid. Quantum yield determinations indicate the photochemical oxidation of such solutions to be a chain reaction. Both the photochemical and the thermal reactions are similarly affected by accelerators and inhibitors so that the same chain mechanism probably applies to both.[225]

In benzene solutions, the absorption spectra of stannic iodide exhibit maxima which indicate a dissociation yielding an unexcited iodine atom at 3650A and an

[218] Morton, D. S., *J. Phys. Chem.*, **33**, 1135 (1929).

[219] Plotnikow, J., and Karschulin, M., *Z. Physik*, **26**, 277 (1926).

[220] Eder, J. M., *Z. Physik*, **37**, 235 (1926).

[221] For a general discussion, see Schömmer, F., *Phot. Rundschau*, **63**, 120, 138 (1926); Elöd, E., and Berczeli, H., *Kolloid-Z.*, **74**, 305 (1936).

[222] Popovitzkiĭ, A., *J. Russ. Phys. Chem. Soc.*, **55**, 1 (1924); *Chem. Abs.*, **19**, 1664 (1925).

[223] Galinsky, A., *Biochem. J.*, **24**, 1706 (1930).

[224] Kantzer, M., *Bull. soc. franc. phot.*, **20**, 167 (1933); *Chem. Abs.*, **28**, 4982 (1934); *Compt. rend.*, **196**, 1882; **198**, 1226 (1934); **201**, 1030 (1935).

[225] Haring, R. C., and Walton, J. H., *J. Phys. Chem.*, **37**, 375 (1933).

excited one at 2850A. In ethyl alcohol, the latter dissociation occurs at 2950A. In methyl alcohol, no maxima are evident.[226]

Certain stannic acids produced either as a result of changes occurring in gelatinous orthostannic acid or formed by the action of nitric acid on tin, acquire a blue coloration on exposure to the ultraviolet rays of sunlight in the presence of certain organic reducing agents, as tartaric, citric and oxalic acids or ethanol. This action is irreversible and is accompanied by decomposition of the reducing agent without visible evolution of gas. The blue color is stable and permanent in the absence of air. The latter destroys the color. Under the same conditions, orthostannic acid does not give the coloration.[227]

According to Harada,[228] the formation of the substance $((CH_3)_3Sn)_2O\cdot(CH_3)_3SnI\cdot H_2O$, by the action of sunlight on tin trimethyl iodide (trimethyliodostannane), does not take place unless tin tetramethyl is present.

Mercury and Its Compounds. About 1924-5, Miethe[229] and Stammreich[230] claimed to effect the transformation of mercury into gold by the use of a new type of mercury vapor arc with very high energy input. Nagaoka, of Tokyo,[231] independently made similar claims, which for a time were accepted by Haber. Miethe believed he had obtained one part of gold from 100,000,000 parts of mercury, and Nagaoka, by passing high tension sparks between pure tungsten points and mercury under paraffin, claimed to have increased the yield ten thousand times. A sample of gold prepared by the latter is said to have been placed in the American Museum of Natural History.[232] Hönigschmid and Zintl[233] reported Miethe's material to have an atomic weight of 197.26. The claims called forth a number of papers,[234] some of which contained further confirmatory claims and others of which speculated as to the nature of the intranuclear transformations. The Siemens Works attempted the bombardment of mercury surfaces by electrons in high vacuum, and even patented certain processes for effecting the transformation.[235]

Doubts were soon raised on many sides. Tiede, Schleede and Goldschmidt,[236] found that mercury purified by two vacuum distillations was free of gold and gave no gold by Miethe's process and Aston[237] rejected the claims on theoretical grounds. Many workers subsequently reported failures in attempts to duplicate these experiments.[238] Further discussion of reported transmutations of metals by ultraviolet radiations is unnecessary, since the energies required are greater than are available from the usual sources of ultraviolet.

Ether solutions of mercuric chloride (10 gm.) after exposure to sunlight in sealed bottles for a period of five months formed 3.2 gm. of calomel containing an organic substance; the ether contained hydrogen chloride, aldehydes and chlori-

[226] Grant, M., *Trans. Faraday Soc.*, **31**, 433 (1935).

[227] Billen, F., *Ingenieur chimiste*, **9**, 60 (1925); *Chem. Abs.*, **21**, 1933 (1927).

[228] Harada, T., *Bull. Chem. Soc. Japan*, **2**, 105 (1927).

[229] Miethe, A., *Naturwiss.*, **12**, 597 (1924); *Chem. Abs.*, **18**, 3139 (1924); *Naturwiss.*, **13**, 635 (1925).

[230] Stammreich, H., *Z. anorg. allgem. Chem.*, **148**, 93 (1925); **150**, 350; **158**, 185 (1926).

[231] Nagaoka, H., *Ind. Eng. Chem., News Ed.*, **3**, 1 (1925); *Naturwiss.*, **13**, 682 (1925).

[232] *Science*, **62**, 1617 (1925).

[233] Hönigschmid, O., and Zintl, E., *Naturwiss.*, **13**, 644 (1925).

[234] Retschinsky, T., *Physik. Z.*, **26**, 280 (1925); Bernhardt, F., *Physik. Z.*, **27**, 713 (1926); Gascheler, A., *Z. Elektrochem.*, **32**, 186 (1926); Kaul, L., *Metallbörse*, **14**, 1432; von Antropoff, A., *Z. angew. Chem.*, **37**, 827 (1924).

[235] French P. 598,140 (1925), to Siemens-Werke A.-G.; British P. 243,670, 1925; 247,508, 1925, and 248,318, 1925.

[236] Tiede, E., Schleede, A., and Goldschmidt, F., *Ber.*, **59**, 1629 (1926); Riesenfeld, E., and Haase, W., *Ber.*, **58**, 2828 (1925); Miethe, A., and Stammreich, H., *Ber.*, **59B**, 359 (1926).

[237] Aston, F. W., *Nature*, Dec. 19, 1925; Riesenfeld, E., and Haase, W., *Ber.*, **59**, 1625 (1926).

[238] Piutti, A., and Boggio-Lera, E., *Giorn. chim. ind. applicata*, **8**, 59 (1925); Garrett, M. W., *Nature*, **118**, 84 (1926); *Proc. Roy. Soc.*, **112A**, 391 (1926); Shelton, H., and Estey, R., *Phys. Rev.*, **27**, 515 (1926); *J. Frank. Inst.*, July 22, **1926**; Harkins, W. D., *Science*, **63**, 1636 (1926); Duhme, E., and Lotz, A., *Ber.*, **59**, 1649 (1926); Haber, F., Jaenicke, J., and Matthias, F., *Ber.*, **59**, 1641 (1926); *Z. anorg. Chem.*, **153**, 153 (1926); Wolfers, F., *J. chim. phys.*, **24**, 727 (1927).

nated compounds.[239] Pougnet[240] exposed a solution of mercuric chloride in a quartz tube to a mercury vapor lamp. He found that the tube became cloudy almost immediately because of the formation of calomel. After thirty minutes, 42 per cent had been decomposed and the calomel began to darken. After seventy minutes, when the decomposition reached 48 per cent, the reaction ceased, indicating the reaction to be reversible.

In solutions of mercuric chloride of relatively low concentration the photochemical reduction by ferrous chloride goes at a rate nearly independent of the concentration of the ferrous salt.[241] For a given concentration of the latter, the rate increases at first with the amount of mercuric chloride and then diminishes. The maximum rate appears to be attained when the salts are present in equimolar quantities (3 molar). Under these conditions, oxygen does not affect the reaction, but when there is a large excess of ferrous chloride, it reduces the quantity of calomel obtainable. The most effective wave-lengths appeared to be shorter than 2650A.

When an alcoholic solution of hydrogen sulfide is gradually added to mercury halides in suspension or in solution, complex compounds of the general formula $HgX_2\cdot 2HgS$ result. These compounds, of various shades of red and yellow, readily undergo a color change in direct or diffuse daylight, regaining their original colors in darkness.[242]

Mercuric iodide, in solutions less than 1.5 molar in potassium hydroxide, is converted into the unstable dark red $HgI_2\cdot HgO$, which decomposes into mercuric oxide, but is unaffected by light.[243] In more alkaline solutions (2-6 molar), there is formed a white complex, $3HgI_2\cdot HgO\cdot 3KOH$, which is decomposed into HgO by light. In solutions stronger in alkali than 7 molar, there is formed a white complex, $HgI_2\cdot 2(\text{or } 3)HgO\cdot XKOH$ which, when dried, is slowly decomposed by light.

Lüppo-Cramer[244] finds that red mercuric iodide present with gum arabic in a gelatin film is light- and color-sensitive, forming a developable latent image.

Cinnabar is blackened by ultraviolet light,[245] but the nature of the reaction has not yet been explained. Cropp[246] attributed it to a decomposition into the elements.

Mercurous sulfate also darkens rapidly and independently of the presence of air. Skinner[247] does not believe there to be production of mercury and mercuric salt and suggests that a dark subsalt or a polymeric modification may be formed.

Halogen mercury thiocyanates are phototropic, and complex halides of mercury such as HgIBr, HgICl and HgBrCl, are somewhat less so.[248]

Cobalt and Nickel. The differences in color of aqueous cobalt salts under

[239] Puxeddu, E., *Gazz. chim. ital.*, **59**, 160 (1929).

[240] Pougnet, J., *Compt. rend.*, **161**, 348 (1915); *J. Soc. Chem. Ind.*, **34**, 1053 (1915).

[241] Winther, C., *Z. wiss. Phot.*, **11**, 60 (1912); *Chem. Abs.*, **6**, 2042 (1912).

[242] Varalalu, T., Ram, A., and Rao, B., *J. Sci. Assoc. Maharajah's College, Vizianagaram*, **1**, 107 (1924); *Chem. Abs.*, **18**, 3529 (1924).

[243] Montignie, E., *Bull. soc. Chim.*, **2**, 290 (1935); *Brit. Chem. Abs.*, **A**, 458 (1935).

[244] Lüppo-Cramer, *Phot. Korr.*, **65**, 97 (1929); *Chem. Abs.*, **25**, 885 (1931).

[245] Brosset, C., *Naturwissen.*, **24**, 813 (1936).

[246] Cropp, W., *Proc. Austral. Inst. Met.*, No. **52**, 259 (1923).

[247] Skinner, S., *Proc. Cambr. Phil. Soc.*, **12**, 260 (1904); *J. Chem. Soc.*, **86**, ii, 173 (1904).

[248] For further discussions of phototropy in other complex mercury compounds, see Rao, S. V. R., and Watson, H. E., *J. Phys. Chem.*, **32**, 1354 (1928), and Rao, E. L., Varahalu, K., and Narasimhaswami, M. V., *Nature*, **124**, 303 (1929). Slight decomposition is believed to account for the yellow to brown color formed on the irradiation of mercury fulminate by A. Borocco, *Compt. rend.*, **207**, 166 (1938).

various conditions have been the subject of a great number of investigations, but these lie beyond the scope of the present text.[249]

Baly [250] finds that on exposure to daylight in the air, nickel carbonate reversibly darkens in color, due to the production of Ni_2O_3 or nickel hydroxide. Extraction of the blackened material with warm water yielded a small amount of formaldehyde, and on evaporation of the filtrate, it was claimed that there were found the nickel salts of some organic acids and some carbohydrate. Similar results were obtained also, it was claimed, with cobalt carbonate.

Cobalt trinitrotriammine in acid solution decomposes completely to cobaltous salts both in light and in darkness. In the dark reaction, there are two stages, each being a unimolecular process. The intermediate product is light-sensitive, radiations of 3660A causing decomposition with a quantum yield of 0.37.[251] On the other hand, the photodecomposition of the cobalt trinitrotriammine appeared to take place in one stage, the velocity, unlike that of the dark reaction, being independent of the acid concentration. The quantum yield is 0.2 (3660A) and the temperature coefficient 1.03 for the velocity.

On illumination of a solution of racemic $K_3Co(C_2O_4)_3$ by dextrocircularly polarized light (5890A), the cobalt compound becomes levorotatory.[252] The decomposition of this compound (0.02-0.002M) by 4360, 4050, 3660 and 3130A is a reaction of zero order, according to Murgulescu,[253] who formulates it

$$Co(C_2O_4)_3 + h\nu \longrightarrow CO(C_2O_4)_2 + (C_2O_4)'$$
$$Co(C_2O_4)_3''' + (C_2O_4)' \longrightarrow (C_2O_4)'' + 2CO_2 + Co(C_2O_4)_2''$$

in agreement with Jäger and Berger, but not with Vranek.[254]

The hydrolysis of aqueous solutions of hexamminecobaltic chloride, nitroamminecobaltic chloride, *cis* and *trans*-dinitrotetrammine cobalt, the two forms of trinitrotriamminecobalt, and *cis*-tetranitrodiamminecobalt are greatly accelerated by light.[255] The cobalt separates, except from dilute solutions in which it remains as sol, as brownish-black cobaltic hydroxide, nitrite ions remaining in the solutions. The photochemical decomposition of all these nitritoamminecobalt compounds is an irreversible reaction of the first order in which the wave-length 3660A is most active. Increase in the number of nitro-groups in the nucleus diminishes the photochemical stability; trinitrotriamminecobalt occupies an intermediate position because of its electrically neutral nucleus. Among stereoisomeric salts, the *trans* compound is the more stable. The velocity of reaction is about one and one-half times as great in acid as in neutral solutions, but is largely independent of the pH. According to Schwarz and Tede,[256] the stability of the complex nucleus diminishes with increasing electroaffinity of the coördinately united anion, in the decreasing order, carbonate, oxalate, nitrite, bromide, chloride, sulfate. The inverted position of the oxalate and nitrite ions is attributed to stereo-

[249] Mazetti, C., *Gazz. chim. ital.*, **56**, 589, 595 (1926); Hantzsch, A., *Z. anorg. Chem.*, **159**, 273 (1927); Vaillant, P., *Compt. rend.*, **189**, 747 (1929); Brode, W. R., *Proc. Roy. Soc.*, **118A**, 286 (1928); Brode, W. R., and Morton, R. A., *ibid.*, **120A**, 21 (1928); Brdicka, R., *Collection Czechoslov. Chem. Comm.*, **2**, 545 (1930); *Chem. Abs.*, **25**, 467 (1931); Howell, O. R., and Jackson, A., *Proc. Roy. Soc.*, **142A**, 587 (1933); Macwalter, R. J., and Barratt, S., *J. Chem. Soc.*, 517 (1934).

[250] Baly, E. C. C., *Phot. J.*, **72**, 474 (1932).

[251] Luther, R., and Frieser, H., *Z. Elektrochem.*, **36**, 141 (1930).

[252] Tsuchida, R., Nakamura, A., and Kobayashi, M., *J. Chem. Soc. Japan*, **56**, 1335 (1935); *Brit. Chem. Abs.*, **AI**, 318 (1937).

[253] Murgulescu, I. G., *Bul. soc. stiinte Cluj*, **8**, 193 (1935); *Chem. Abs.*, **30**, 4402 (1936).

[254] Vranek, J., *Z. Elektrochem.*, **23**, 340 (1917).

[255] Schwarz, R., and Weiss, H., *Ber.*, **58**, 746 (1925).

[256] Schwarz, R., and Tede, K., *Ber.*, **60**, 63 (1927).

chemical factors and probable ring formation in the case of the oxalato-residue. In the cobaltpentammine series, the sequence is carbonate, chloride, oxalate, sulfite, nitrite, nitrate (equal to sulfate). The exceptional position of the chloride ion is due to its non-complex character. The presence of water molecules in the complex increases the tendency to hydrolyze. The complex compounds of chromium are less stable and more subject to photochemical change than are those of cobalt.

Tungsten and Molybdenum. The light-sensitivity of the reduction of tungstic acid by glucose to a blue product was studied by Vasilief-Sinzova.[257] The reduction appeared to follow a monomolecular course. The light-sensitivity of freshly prepared solutions of tungstic acid increases with increase of the concentration of added hydrochloric acid up to 0.47 normal, and then decreases, perhaps because the number of molecules of H_2WO_4 sensitive to light increases until the coagulating effect of the acid predominates.

Underlying these observations is the fact that when aqueous solutions of alkali tungstates are gradually acidified, amorphous precipitates of hydrated forms of tungsten trioxide are finally obtained. Before the precipitate is actually formed, polymerization changes occur in the dissolved tungstic acid, hexatungstic acid being first produced. With the addition of more acid there is a further polymerization to metatungstic acid, which is probably a diparatungstic acid, and in the presence of other acids, such as arsenic and phosphoric, heteropolytungstic acids are formed. These changes have been followed by light absorption and diffusion methods.[258] Such reactions have been made the basis of a patent for ultraviolet-sensitive layers suitable for actinometric purposes.[259] The layer contains compounds of molybdenum, tungsten or thallium, together with an oxidizable substance as glucose, made slightly acid by hydrochloric or citric acids. On exposure to wave-lengths shorter than 4000A, the layer changes from white to blue.

Hanzawa [260] described a chemical actinometer using ammonium molybdate in dilute hydrochloric acid containing small quantities of ethanol. Ghosh and Bhattacharya [261] find the photochemical reduction of tungstic and molybdic acid sols by alcohol to be of zero order. The velocity constants were found to decrease in sols which had aged, but the velocity constants of the latter could be increased to values greater than those of fresh sols by heating at 70°C. for eight minutes. In the presence of univalent ions the sols are less light sensitive. According to Sachs,[262] the best method for the preparation of molybdenum blue is the reduction of a solution of sodium molybdate, acidified with hydrochloric acid, by formic acid in the light of a mercury arc. Hydrogen may also serve as the reducing agent.[263]

When exposed to sunlight in a sealed bottle, an ether solution of titanium tetrachloride turned brown during the second day, and ultimately became green. On low temperature evaporation of the solvent, the mixture became violet, suggesting the green and violet modifications of titanium trichloride.

The Rare Earths. Boll [264] studied the rate of hydrolysis of tetrachloro-

[257] Vasilief-Sinzova, A., *J. Chim. Ukraine*, **1**, 425 (1925); *Chem. Abs.*, **20**, 2792 (1926).

[258] Jander, G., Majert, D., and Aden, T., *Z. anorg. Chem.*, **180**, 129 (1929).

[259] Sheppard, S. E., and Eberlin, L. W., U. S. P. 1,934,451, Sept. 11, 1933, to Eastman Kodak Co.; *Brit. Chem. Abs.*, **B**, 873 (1934).

[260] Hanzawa, T., *J. Agr. Chem. Soc. Japan*, **6**, 1093 (1930); *Chem. Abs.*, **25**, 2643 (1931).

[261] Ghosh, S., and Bhattacharya, A. K., *J. Indian Chem. Soc.*, **7**, 717 (1930); *Chem. Abs.*, **25**, 252 (1931); *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 29 (1932); *Chem. Abs.*, **27**, 2097 (1933).

[262] Sachs, D., *J. chim. phys.*, **29**, 474 (1932).

[263] Krauss, F., and Bruchhaus, E., *Z. anorg. allgem. Chem.*, **189**, 53 (1930).

[264] Boll, M., *Compt. rend.*, **156**, 138 (1914); *J. Chem. Soc.*, **104**, ii, 171 (1913). For data on various platinum complexes, see Lifschitz, I., and Froentjes, W., *Z. anorg. allgem. Chem.*, **233**, 1 (1937).

platinic acid when submitted to radiations of different energy, the amount of radiation reaching the solution being controlled by a cell containing a dilute solution of caffeine, the concentration and thickness of the caffeine layer being varied. A later study by Boll [265] of the reaction in very dilute aqueous solution shows the progress of the photochemical reaction by measuring the increase in the electrical conductivity of the solution.

By the action of hydrogen and short ultraviolet rays, Krauss and Bruchhaus [266] reduced a brown solution made by dissolving ruthenium hydroxide in hydrochloric acid to a bright, transparent, orange-colored solution, containing bivalent ruthenium. Colorless liquid ruthenium pentacarbonyl in light evolves carbon monoxide and produces orange-red, pseudo-hexagonal plates of $Ru_2(CO)_9$. The latter, when dissolved in glacial acetic acid become lilac in sunlight.[267]

Ultraviolet light causes the liberation of oxygen from a 0.1 molar solution of ceric perchlorate in molar perchloric acid. The quantum efficiency is at first about 0.1. Since the perchlorate ion is not decomposed, the following mechanism was suggested by Weiss and Porret.[268]

$$Ce^{++++} + h\nu \longrightarrow Ce^{++++}\text{ (excited)}.$$
$$Ce^{++++}\text{ (excited)} + H_2O \longrightarrow Ce^{+++} + H^+ + OH$$
$$OH + OH \longrightarrow H_2O + O$$
$$O + O \longrightarrow O_2.$$

The accumulation of Ce^{+++} retards the reaction, probably by the loss of an electron to the OH molecule with formation of Ce^{++++} and the hydroxyl ion.

Uranium Compounds. Uranium is the only element other than the rare earths, whose compounds exhibit line absorption spectra.[269]

An acid mixture of solutions of sodium hypophosphite and uranyl sulfate remains unchanged in darkness, but when exposed to light, rapidly deposits a green colloidal precipitate containing 54.5-56 per cent of uranium and 15.75-17.5 per cent of phosphorus, and consisting of hypophosphite with some phosphite and phosphate, mixed with sodium phosphate and uranous sulfate.[270]

Frequent examples of the use of uranyl salts as photosensitizers will be found in other chapters, particularly in connection with the photochemical behavior of the organic acids. Rousseau [271] subjected salts or solutions of salts of uranium, manganese, iron or nickel to the action of solar or ultraviolet radiation, and then added the irradiated salts to liquids in which photocatalysis or the sterilization or activation of ferments is to be effected.

Zinc oxide has also been widely employed as a photosensitizer. Winther [272] found that when certain samples of zinc oxide were strongly illuminated, in the presence of air, by light filtered through ordinary glass, a substance appeared in

[265] Boll, M., *Ann. Phys.*, **2**, 54, 266 (1914); *J. Chem. Soc.*, **108**, ii, 123 (1915).

[266] Krauss, F., and Bruchhaus, E., *Z. anorg. allgem. Chem.*, **189**, 53 (1930).

[267] Manchot, W., and Manchot, W. J., *Z. anorg. allgem. Chem.*, **226**, 385 (1936).

[268] Weiss, J., and Porret, D., *Nature*, **139**, 1019 (1937).

[269] Details of the absorption and fluorescence spectra of uranium compounds are given by van Heel, A., *Comm. Phys. Lab. Univ. Leiden, Suppl. No.* **55B** to *Nos.* **169–180** (1925); *Chem. Abs.*, **21**, 3311 (1927); Ephraim, F., and Mezener, M., *Helv. Chim. Acta*, **16**, 1257 (1933); Ghosh, J. C., and Mittra, B. N., *Quart. J. Indian Chem. Soc.*, **4**, 353 (1928); Levshin, V. L., *Bull. acad. sci., U.R.S.S., Classe sci. math. nat., Ser. Phys.*, **No. 2**, 185 (1937); *Chem. Abs.*, **31**, 8380 (1937). For the photochemical liberation of iodine from potassium iodide by uranyl sulfate solutions, see Montignie, E., *Bull. soc. chim.*, **5**, 564 (1938).

[270] Dienert, F., and Villemaine, F., *Compt. rend.*, **199**, 1113 (1934). See also Chretien, A., and Kraft, J., *Compt. rend.*, **204**, 1736 (1937).

[271] Rousseau, E., British P. 226,534, Dec. **13**, 1924; *Brit. Chem. Abs.* **B**, 406 (1926).

[272] Winther, C., *Z. wiss. Phot.*, **21**, **168** (1921).

the gas phase which was capable of oxidizing iodide ion to iodine. In the use of this zinc compound for photosensitization of the decomposition of silver salts to sunlight

$$2AgNO_3 + ZnO \longrightarrow 2Ag + Zn(NO_3)_2 + 1/2O_2,$$

Perret [273] found silver peroxide to be formed as an intermediary product. In the reduction of mercuric chloride to calomel by zinc oxide in sunlight, four to fifteen days were required for a notable transformation; the reaction attained a stationary state. When the reaction is of zero order, it is greatly accelerated by dextrose and by sucrose. In the presence of air, the sensitizing action of zinc oxide on the photolysis of calomel consists in the simultaneous oxidation and reduction of the salt. Bhattacharya and Dhar [274] listed twenty-nine reactions sensitized by zinc oxide, including among others, the separation of gold from its chloride, the oxidation of potassium iodide by potassium persulfate, oxidation of sodium nitrite by iodine, oxidation of hydroxylamine or of hydrazine by iodine, decomposition of mercuric oxide, and decomposition of aqueous solutions of potassium permanganate or of potassium persulfate.

To account for the inactivity of many samples of zinc oxide, Jung and Kunau [275] studied samples prepared by various methods. Only those obtained by roasting the nitrate proved to be active which suggested that a zinc oxynitrate rather than the oxide might be the true photosensitizing agent. McMorris and Dickinson [276] identified nitrogen dioxide as the gaseous product formed in small quantity when zinc oxide (prepared from the nitrate) is strongly illuminated, in a stream of oxygen, by the mercury arc radiations filtered through water and Pyrex glass. Baur [277] held that on the absorption of energy, zinc oxide is converted into a "phototrope," one-half of which is capable of oxidizing a neighboring substance, while the other half reduces the same substance. Such a conception of intramolecular electrolysis is however, unnecessary for the explanation of photosensitization by zinc oxide, since it has been found that a gaseous oxidizing agent is liberated from zinc oxide on irradiation.

[273] Perret, A., *J. chim. phys.*, **23**, 97 (1926).

[274] Bhattacharya, A. K., and Dhar, N. R., *Quart. J. Indian Chem. Soc.*, **4**, 299 (1927); *Chem. Abs.*, **22**, 915 (1928).

[275] Jung, G., and Kunau, E., *Z. physik. Chem.*, **15B**, 45 (1931).

[276] McMorris, J., and Dickinson, R. G., *J. Am. Chem. Soc.*, **54**, 4248 (1932).

[277] Baur, E., *Trans. Faraday Soc.*, **21**, 627 (1925); see also Chapter 16.

Chapter 21

Photochemical Reactions of Inorganic Solids

The present theories of photoprocesses in crystals have resulted from attempts to interpret the experimental studies of the effects of the absorption of light by ionic alkali halide crystals by the methods of quantum mechanics recently developed for the study of the properties of metals.[1] In large part, the experimental foundation has been laid at Göttingen, as an extension of the studies of Gudden and Pohl [2] on the photoconductivity of certain homopolar crystal lattices, notably the diamond. After a number of attempts had been made to obtain similar measurements upon variously colored rock salt crystals,[3] a thorough study was undertaken of the formation by ultraviolet light of a yellow color in alkali halides. This phenomenon had been observed by Goldstein [4] as early as 1896. To obtain an understanding of the nature of this process, Hilsch and Pohl [5] made observations of the far ultraviolet (including the Schumann region) absorption spectra of a number of alkali halides. In some cases, the halides were deposited upon quartz plates by vacuum sublimation. It was found that the nature of the absorption was determined primarily by the halogen ions, and was relatively but little influenced by the nature of the cation. The extinction curves showed definite sharp maxima. Absorption in these bands was believed to effect a transfer of an electron from a halogen ion of the crystal lattice to an adjacent metal cation, producing free halogen and metal atoms. In each case, the band of longest wave-length (corresponding to the absorption of the smallest effective quantum) was attributed to the liberation of the atoms in their normal states. The energy required for this was at first held to be equal to, first, that required to separate an electron from a halogen ion (its electron affinity E) and, second, that required to overcome the coulombic attraction between the sodium and halogen ions (the coulombic part of the lattice energy of the crystal Q). This energy requirement would be diminished by the work necessary to ionize the alkali atom (its ionization potential I), since this energy is liberated when the ion is converted into the atom. From available data, the values of $Q+E-I$ were calculated for the various halides studied. The correspondence between the calculated energy values and the energy corresponding to the first absorption maxima was only fairly satisfactory. The value calculated for the mean of the lithium, sodium, potassium and caesium iodides was 5.76 electron-volts and the observed value was 5.56 electron-volts.[6, 7]

[1] Bloch, F., *Z. Physik,* **52,** 555 (1928); **59,** 208 (1930); Wilson, A. H., *Proc. Roy. Soc. London,* **133A,** 458 (1931); **134A,** 277 (1931); Peierls, R., *Ann. Physik,* **4,** 121 (1930).

[2] Gudden, B., and Pohl, R., *Z. Physik,* **16,** 170 (1923); **17,** 331 (1923).

[3] Gyulai, Z., *Z. Physik,* **32,** 103 (1925); **35,** 411 (1926); Flechsig, W., *Ibid.,* **46,** 788 (1928).

[4] Goldstein, E., *Z. Instrdke,* **16,** 211 (1896).

[5] Hilsch, R., and Pohl, R. W., *Z. Physik,* **57,** 145 (1929); **59,** 812 (1929); **64,** 606 (1930); **68,** 721 (1931). For earlier observations, see Pfund, A. H., *Phys. Rev.,* **32,** 39 (1928) and for other halides, Ottmer, R., *Z. Physik,* **46,** 798 (1928).

[6] See also Bonhoeffer, K., and Harteck, P., "Grundlagen der Photochemie," p. 141, Dresden, T. Steinkopff; Sponer, H., "Molekülspektren und Ihre Anwendung auf Chemisch Probleme," II, 339-361, Berlin, J. Springer. de Boer, J. H., "Electron Emission and Adsorption Phenomena," Cambridge Univ. Press, 1935, 239.

The absorption maxima at shorter wave-lengths were attributed to the liberation of the elements in excited states. The difference between the first and second maxima in the spectra of the iodides of alkalies other than caesium, expressed in volts, was 1.02. That between the $^2P_{3/2}$ and $^2P_{1/2}$ states of the iodine atom is, from atomic spectra, 0.937 volt. In the case of the bromides, the corresponding values were 0.52 volt from the separation of the absorption maxima of the crystals and 0.454 volt from atomic spectra.

The third maximum observed in the iodide spectra was attributed to the production of a normal halogen and an excited alkali atom. The caesium halides are exceptional, since in these the crystal structure is different. Two extra maxima appear in caesium iodide.

The yellow coloration produced by irradiation in the absorption bands of the halides or by the action of x-rays was attributed to the production of alkali metal atoms, the formation of which is analogous to that of the latent image in the case of silver bromide. The yellow color [8] produced by irradiation of sodium chloride crystals corresponds to an absorption maximum at 4650A. This induced coloration is but slight and it is said that but few color centers are usually formed. Longer exposures or the use of more intense light sources fail to increase greatly the yield of color centers. The yields of these color centers as determined by absorption measurements give rather definite information regarding the quantum yields of the primary photoprocess. Such information can but rarely be obtained in the study of photochemical processes conducted in gaseous or liquid systems. In crystals at room temperatures, Smakula [9] found that during irradiation with very low light intensities (few quanta), the yield approached unity. With more intense irradiation, however, a condition of saturation was reached, the quantum yield dropping below unity. Under these conditions, the electron displaced was believed to return to its original location. When low intensities were used, the fewer electrons displaced throughout the crystal were thought to be able to acquire energy from the thermal motion of the crystal lattice. This energy lessened their chances of regaining their initial states.

It soon became evident that this relatively simple picture of the processes occurring in an ionic crystal required modification. The absorption of the induced color centers was observed to differ from that of the same alkali atoms in the vapor phase. It was found to be dependent upon the nature of the lattice in which the atoms were believed to be liberated. Thus, the induced maximum for the sodium salts lies at 3480A in the fluoride, at 4650A in the chloride and at 5400A in the bromide. Mollwo [10] finds the color center frequency to be inversely proportional to the square of the lattice constant. It may be displaced toward longer wave-lengths by an increase of temperature. It has also been found that the formation of appreciable amounts of the latent image or so-called F color centers depends upon the presence of defects in the lattice. The more perfect the crystal, the lower are the yields of the latent image, the electron immediately returning to the halogen atom after it has been displaced by absorption unless the energetic

[7] Born, M., [*Z. Physik,* **79,** 62 (1932)] raised certain objections to the calculation of the wave-length of the first maximum, but it has been suggested that these may be overcome by taking into account polarization effects in the calculations of the lattice energies. See also, Klemm, W., *Z. Physik,* **82,** 529 (1933); Fues, E., *Ibid.,* **82,** 536 (1933); Mayer, J. E., *J. Chem. Physics,* **1,** 270 (1933).

[8] This must be distinguished from the blue color of certain samples of rock salt which is due to the presence of colloidally dispersed sodium. Phipps, T. E., and Brode, W. R., *J. Phys. Chem.,* **30,** 507 (1926); Leroux, P., *Compt. rend.,* **188,** 904 (1929).

[9] Smakula, A., *Z. Physik,* **63,** 762 (1930).

[10] Mollwo, E., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse,* **1931,** 97; **1932,** 254; *Chem. Abs.,* **26,** 5847 (1932); **27,** 665 (1933). Fröhlich, H., *Z. Physik,* **80,** 819 (1933).

conditions are modified by the presence of lattice defects, foreign atoms or surface irregularities. Smekal [11] has employed the localization of the color centers induced by irradiation as a means of studying the ultramicroscopic crevice imperfections of crystals.

The influence of the lattice structure upon the phenomenon is particularly emphasized in the newer theoretical approach to the problem. This is based upon a consideration of the energy levels of the crystal as a whole rather than of the energy levels of the isolated metal and halogen atoms or ions. The modifications in the potential energy diagrams of the isolated atoms which result when they are made to approach each other to the distances in the crystal lattice are developed mathematically. In this way there may be obtained a model analogous to that which has proved useful in recent work on the structure of metals. Such a model provides a potential energy diagram for an electron moving in the periodic force fields of a lattice.[12] Although the mathematical methods employed in this approach can be comprehended only by specialists, mention may be made of some of the results to which they have led. The sharp energy levels of the individual atoms are, in the crystal, transformed into broad bands or zones, each of which can accommodate the number of electrons required to fill in the corresponding energy level of each of the atoms in the lattice. Within each such continuous zone there are an almost infinite number of energy levels. For this reason, if a zone is only partially filled with the number of electrons which the zone can hold, these electrons are free to move as in a metal. In the alkali halide crystals, ions rather than atoms are present, since the halogen atoms have acquired from the metal atoms their loosely bound valence electrons. This means that the zone corresponding to the 4P level of the halide, *e.g.*, bromine, ions is filled with electrons.[13] On the other hand, the zone of higher energy level of the metal ions is empty (at 0°K). If by heat or light, electrons could be raised into this zone to partially fill it, these electrons would also be able to move freely throughout the crystal and render it conducting. Between these two zones there is a wide region of forbidden energy levels. In actual rather than ideal crystals, there may be additional energy levels situated just below the upper conducting energy zone. These may be due to the presence of lattice irregularities or to surface effects.

According to current theories, the color centers produced by the action of ultraviolet light or x-rays upon the alkali halide crystals are due to the presence of electrons in these localized energy levels below the conduction zone. Irradiation is believed to raise electrons to these levels from a lower level, *e.g.*, of a halide ion, by a two-stage process. It is first raised to a higher level which may or may not lie within the conducting zone. From this it drops back to the final level somewhat below the upper conducting zone. Electrons in this level are responsible for the absorption exhibited by the "latent image" or F centers. The F color centers can also be produced by directly introducing electrons from a pointed cathode [14] or by heating the crystals in an alkali metal vapor. Since different metal vapors produce the same coloration in a crystal, it appears that it is the

[11] Smekal, A., *Physik. Z.*, **33**, 204 (1932); de Boer, J. H., *Rec. trav. chim.*, **56**, 301 (1937). See also, Lorenz, H., *Fortschr. Mineral., Krist. Petrog.*, **20**, 290 (1936); Blochinzew, D., *Physik. Z. Sowj.*, **10**, 431 (1936).

[12] Gurney, R. W., *Proc. Roy. Soc. London*, **141A**, 209 (1933); Morse, P. M., *Phys. Rev.*, **35**, 1310 (1930); Brillouin, L., *J. physique*, **1**, 377 (1930); Kronig, R., and Penney, W. G., *Proc. Roy. Soc. London*, **130A**, 499 (1931).

[13] See, for further discussion, Webb, J. H., *J. Opt. Soc. Am.*, **26**, 367 (1936).

[14] Stasiw, O., *Nachr. Ges. Wiss. Göttingen Math.-physik. Klasse*, **1932**, 261; Gurney, R. W., *Proc. Roy. Soc. London*, **141A**, 209 (1933).

electrons rather than, as previously supposed, the neutral atoms which are, in some manner, responsible for the color acquired by the crystals.

Hilsch and Pohl [15] showed that heating a crystal with F centers in hydrogen causes their gradual disappearance. At the same time a new absorption band (U band) in the ultraviolet near the long wave-length edge of the characteristic absorption band appears. The same process can be effected, although very inefficiently, by the absorption of light by the F centers. The U centers can also be produced by passing an electric current from the liquid to the crystals during their formation from the fused halide. The absorption of ultraviolet light by the U centers of the crystal reverses the optical process by which they can be formed from the F centers. As the U centers are destroyed, the F centers reappear in a one-to-one correspondence. The U centers were believed due to electrons in discrete energy levels slightly above the lower filled zone. The energetic relations between the upper conductance zone, the lower filled zone and the discrete levels representing the F and U centers have been summarized in a potential energy diagram by Tartakowsky [16] for the sodium chloride crystal. The filled and conductance zones are separated by 7.7 electron-volts, quanta of this magnitude being required to render pure crystals conducting. The F centers lie 2.65 electron-volts below the upper zone, and the U centers, 1.3 electron-volts above the lower zone.

More recently, Hilsch and Pohl [17] suggest that U centers result from the diffusion of hydrogen into the crystal and that alkali hydride molecules are formed.

A large number of investigations deal with the effects of the absorption of light by the U and F centers in crystals at various temperatures. These are primarily of physical rather than chemical interest, since they are concerned in part with photoelectric phenomena and in part, particularly in the case of crystals with foreign atom impurities, with phenomena of phosphorescence and luminescence.[18] These latter provide a basis for understanding the technically important use of luminescent substances in lighting and television. As such, they lie beyond the scope of this work.[19]

Another feature which has emerged from the use of quantum mechanics in the treatment of the absorption of light by crystals is a recognition of the fact that light energy absorbed in one portion of a crystal may be propagated throughout the lattice as an excitation wave. In other words, the excited electron and the hole it has left in the lower band may be conceived as moving about the crystal. This excitation wave may be considered, in terms of the de Broglie wave-theory of matter, as a particle called an "exciton" which moves through the crystal. This term was introduced by Frenkel in a mathematical treatment of the degradation and migration of energy in crystals.[20] Franck and Teller [21] discuss the signifi-

[15] Hilsch, R., and Pohl, R. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1933**, 322, 406; *Chem. Abs.*, **29**, 3237 (1935); *Z. Physik*, **87**, 78 (1933); *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe* II, **1**, 209 (1935); *Chem. Abs.*, **30**, 4763 (1936).

[16] Tartakowsky, P., *Z. Physik*, **90**, 504 (1934); Tartakowsky, P., and Poddubny, W., *Ibid.*, **97**, 765 (1935).

[17] Hilsch, R., and Pohl, R. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe* II (N.F.), **2**, 139 (1936); *Chem. Abs.*, **31**, 7754 (1937); *Trans. Faraday Soc.*, **34**, 88 (1938).

[18] Hughes, A. L., *Rev. Mod. Phys.*, **8**, 294 (1936). Much of the preceding discussion has been based upon this review.

[19] For reviews, see Pohl, R. W., *Kolloid-Z.*, **71**, 257 (1935); *Proc. Phys. Soc. London*, **49**, No. 274, 3, 36 (1937); *Abhandl. Ges. Wiss. Göttingen, Math.-physik. Klasse, III*, **18**, 71 (1937); Leverenz, H. W., and Seitz, F., *J. Applied Phys.*, **10**, 479 (1939); Symposium in *Trans. Faraday Soc.*, **35**, 1 (1939).

[20] Frenkel, J., *Physik. Z. Sowj.*, **9**, 158 (1936); *Phys. Rev.*, **37**, 17, 1276 (1931); Peierls. R.. *Ann. Physik*, **13**, 905 (1932).

[21] Franck, J., and Teller, E., *J. Chem. Phys.*, **6**, 861 (1938).

cance of this concept in the treatment of photochemical processes induced at locations of a crystal (surfaces or disturbed lattice points) at a distance from the point at which light absorption occurs.

The Silver Halides and the Photographic Latent Image

Present concepts of the latent image [22] are in general analogous to those developed in the treatment of the alkali halides. The importance of the photographic process led to a large amount of early work. It was indeed shown by many [23] prior to the work on the alkali halides that the primary photographic process takes place in a halogen ion rather than in silver. Before considering the recent interpretations, brief reference will be made to some of the earlier observations on the products resulting from the prolonged irradiation of the silver halides. It is interesting to recall that the existence of ultraviolet rays was first made known by the demonstration by Ritter of the ability of invisible radiations beyond the blue end of the solar spectrum to blacken silver chloride. Ritter [24] also showed that their effect could be reversed by the action of other invisible rays beyond the red. Since the absorption spectra of the bromide and iodide of silver extend into the visible, most studies have been concerned with the effects of visible light.

For a time it was considered, notably by Becquerel and by Carey-Lea, that the initial product of the action of light (latent image) was some subhalide of silver. By the study of artificial photohalides prepared by mixing and simultaneously coagulating silver and silver halide hydrosols, Lüppo-Cramer cast doubt upon this. Many were the attempts to prove or disprove the existence of definite photohalides by direct quantitative measurements of the halogen evolved during prolonged irradiation of silver halides. Richardson [25] found 8 per cent of the total halogen to be liberated when 26 gms. of silver chloride under water was exposed to sunlight. Baker,[26] however, found only 14 mg. of chlorine to be evolved from 51 gms. of silver chloride after a considerable exposure to light. By the use of a special balance, Volmer [27] found silver bromide to lose as much as 40 per cent of its bromine on illumination. Negative results having been recorded by Strömberg [28] and by Koch and Schrader,[29] a careful reinvestigation was made by Hartung.[30] By the use of silver bromide films on silvered vitreous silica supports on a special microbalance, he found a maximum loss of 96 per cent of the total halogen. Similar results were obtained with silver chloride. Studies of the rate of rebromination of thin silver films gave no evidence of the formation of silver subbromides. This work definitely favored the hypothesis that the formation of the latent image involves the formation of free silver.

In other attempts to solve this problem, varied techniques as microscopic studies of the effects produced by light,[31] or the alteration of the silver halide x-ray diagram [32] have been employed. The latter method gave indications of the formation of crystalline silver. The influence of various ions adsorbed on silver chloride on the liberation of chlorine by light has been studied by Schwarz and Dieffenbacher.[33] In their experiments,

[22] Webb, J. H., *J. Opt. Soc. Am.*, **26**, 367 (1936); "Proc. 6th Summer Conference (at Mass. Inst. Technology) on Spectroscopy and Its Applications," p. 157, New York, John Wiley and Sons, 1939; Gurney, R. W., and Mott, N. F., *Proc. Roy. Soc. London*, **164A**, 151 (1938).

[23] Fajans, K., and Frankenburger, W., *Z. Elektrochem.*, **28**, 499 (1922); Sheppard, S. E., and Trivelli, A. P. H., *J. Phys. Chem.*, **29**, 1568 (1925).

[24] Ritter, *Nicolson's J.*, **8**, 214 (1804).

[25] Richardson, A., *J. Chem. Soc.*, **59**, 536 (1891).

[26] Baker, H. B., *Ibid.*, **61**, 728 (1892).

[27] Volmer, *Diss.*, Leipzig, **1910**, 41. Cited by Hartung.

[28] Strömberg, R., *Z. wiss. Phot.*, **22**, 165 (1924); *Chem. Abs.*, **17**, 3838 (1923).

[29] Koch, P. P., and Schrader, F., *Z. Physik*, **6**, 127 (1921); Koch, P. P., and Kreiss, B., *Ibid.*, **32**, 384 (1925).

[30] Hartung, E. J., *J. Chem. Soc.*, **125**, 2198 (1924); **121**, 682 (1922); **127**, 2691 (1925); **1926**, 1349.

[31] Trivelli, A. P. H., and Sheppard, S. E., *J. Phys. Chem.*, **29**, 1568 (1925).

[32] Koch, P. P., and Vogler, H., *Ann. Physik*, **77**, 495 (1925); Trillat, J. J., and Motz, H., *J. Phys. Radium*, **7**, 89 (1936).

[33] Schwarz, R., and Dieffenbacher, K., *Z. anorg. Chem.*, **152**, 91 (1926).

50 mole per cent of a foreign nitrate solution was added to a silver nitrate solution which was then precipitated by an amount of sodium chloride less than sufficient to throw out all of the silver chloride. The acetate, citrate, tartrate, tetraborate and sulfate anions did not affect the rate of photodecomposition, but copper, lead, barium and thallium reduced the decomposition to 33, 32, 68 and 29 per cent, respectively, of that of silver chloride with only silver ions adsorbed.

More recently, attempts have been made to determine quantum yields for the photolysis of silver chloride. For exposures involving total absorption of the 3650A line, Feldmann and Stern [34] found a quantum yield of 0.86. The irradiation was conducted under water and the liberated chlorine determined by titration. Subsequently, they found [35] for the 3130A line a value of unity. The silver chloride used had been precipitated in the presence of sodium nitrite. The latter served to combine with the liberated chlorine and lessened the probability of a reversal of the photolysis. With more compact samples of silver chloride, the quantum yield was, however, only 0.13 in the presence of sodium nitrite and 0.20 in its absence. For precipitated silver bromide with sodium nitrite, the 3650 and 4360A lines gave yields of unity, but for silver bromide precipitated in the absence of sodium nitrite and for crystallized silver bromide in the presence of a nitrite, the yield was only 0.4. Rather similar or lower values had been reported previously by others.[36]

The yield may be affected not only by the compactness of the material, which alters the probability of the reverse reaction, but also in long continued experiments by absorption of some of the light by liberated silver atoms. MacMahon and Chatterji [37] measured the absorption of oxygen by irradiated silver bromide and chloride in a tube containing gold as halogen acceptor. The oxygen is absorbed by the dispersed silver resulting from the photolysis.

During the formation of the latent image, the silver halides exhibit photoconductivity. The absorption band of silver bromide in the visible has a minimum energetic separation from the unfilled upper conductance band of the order of three electron-volts. Electrons raised into this band give rise to conductance.[37a] An approximate agreement between the sensitivity curves for photoconductance and for the photographic effects was observed by Arrhenius,[38] indicating according to present conceptions, that the liberation of an electron by light absorption may be concerned also with the formation of the latent image. Some discrepancies between the curves were noted by Coblentz,[39] but Toy [40] and co-workers explain these as due to the fact that the photoconductance experiments were made on large pure silver bromide crystals and the photographic ones on fine crystals in gelatin. Sheppard and Vanselow [41] calculated that the photoelectrons have in the lattice a mean free path of the order of 10^{-6} cm.

[34] Feldmann, P., and Stern, A., *Naturwiss.*, **16**, 539 (1928); *Z. physik. Chem.*, **12B**, 449, 467 (1931).

[35] *Z. physik. Chem.*, **26B**, 45 (1934). See, however, Plotnikow, I., *Phot. Korr.*, **67**, 199 (1931); *Chem. Abs.*, **26**, 1861 (1932).

[36] Eggert, J., and Noddack, W., *Z. Physik*, **31**, 922, 942 (1925); Eggert, J., *Z. Elektrochem.*, **32**, 491 (1926).

[37] MacMahon, P. S., and Chatterji, A. C., *Proc. 15th Indian Sci. Congr.*, **1928**, 138; *Chem. Abs.*, **25**, 2922 (1931).

[37a] For a quantum-mechanical treatment of conductance, see Fowler, R. H., *Proc. Roy. Soc. London*, **140A**, 505 (1933); **141A**, 56 (1933).

[38] Arrhenius, S., *Sitzb. Akad. Wiss. Wien*, **96**, 831 (1887); Scholl, H., *Ann. Physik*, **16**, 193, 417 (1905); Wilson, W., *Ibid.*, **23**, 107 (1907).

[39] Coblentz, W. W., *Bur. Standards Bull.*, **18**, 489 (1922). This section is based in part upon a review by Webb, J. H., *J. Opt. Soc. Am.*, **26**, 367 (1936).

[40] Toy, F. C., *Nature*, **120**, 441 (1922); *Proc. 7th Intern. Congr. Phot.*, 14 (1928); Toy, F. C., and Harrison, G. B., *Nature*, **123**, 679 (1929); *Proc. Roy. Soc. London*, **127A**, 613, 629 (1930).

[41] Sheppard, S. E., and Vanselow, W., *J. Phys. Chem.*, **33**, 250 (1929); Sheppard, S. E., *Phot. J.*, **60**, 397 (1928).

As in the case of the alkali halide crystals, the formation of the latent image may be demonstrated optically. The absorption spectrum of silver bromide extends from about 4700A to the shorter wave-lengths and exhibits a maximum at about 2200A. It differs from the spectra of the alkali halides in lacking sharp maxima and minima, although there are indications of their existence. The latent image formed by exposures to the low intensities ordinarily used in photography is not visible, but Hilsch and Pohl [42] showed that by the use of thicker crystals and greater exposures it could be detected as an induced band in the infrared with a maximum at 6900A. The absorption spectra of the original crystal and that of the latent image may partially overlap and that of the latent image may tend to become complex as compared with those encountered in the alkali halides. This may be ascribed to a tendency for the liberated silver atoms to become coagulated.[43] Hilsch and Pohl calculated from dispersion theory and the observed absorption of the latent image that in both the photographic plate and in irradiated alkali halide crystals, the latent image is due to a concentration of but one color center in 10^6 to 10^7 salt molecules. The quantum yield amounts to about 0.33 to 0.4 color centers per photon under the usual exposure conditions. Blair and Leighton [44] have given an equation expressing the rate of formation of the latent image.

It has been assumed recently that the latent image corresponds in a general way to the F centers of the alkali halides. According to this view the latent image would represent electron energy levels rather than silver atoms. The manner in which such electronic excitation levels occasion the liberation and coagulation of silver atoms is as yet speculative.[45]

Theories of Sensitivity. It has been stated that the light-sensitivity of the silver halides does not coincide with their absorption curves, since it has a maximum in the short visible, and drops off in the ultraviolet where the absorption curve is still rising rapidly. A small hump observed by Fesefeld [46] at about 4300A in the absorption spectrum of silver iodide does, however, coincide with the region of maximum sensitivity of that salt. There is also some discrepancy between the long-wave thresholds for absorption and photographic action. In part this may be due to the fact that methods for detecting the formation of a latent image by subsequent development are more sensitive than those for measuring the silver halide light absorption curve. Before the development of the theories discussed in connection with the alkali halides, attempts were made to relate the sensitivity threshold to the energy required to remove electrons from the halogen ions of the normal crystal lattice. Wave-lengths longer than those calculated proved, however, to be effective. Frankenburger and Fajans [47] suggested that submicroscopic flaws in the crystal lattice might serve to lessen the energy required. Pauling [48] proposed to calculate the threshold wave-length by deducting from the sum of the electron affinity of the halogen and the coulombic energy of the lattice

[42] Hilsch, R., and Pohl, R. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse,* **1930,** No. 2, 176; *Chem. Abs.,* **25,** 884 (1931); *Z. Physik,* **64,** 606 (1930). For analogous results on silver halide grains, see Kirillow, E. A., *Z. wiss. Phot.,* **26,** 235 (1929); *Chem. Abs.,* **23,** 1829 (1929); Eggert, J., and Schmidt, R., *Z. Physik,* **48,** 541 (1928).

[43] See Löhle, F., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse,* **1933,** 271; *Chem. Abs.,* **28,** 973 (1934); Savost'yanova, M. V., and Toporetz, A., *Compt. rend. acad. Sci. (U.R.S.S.),* **2,** 225 (1934); *Chem. Abs.,* **28,** 5340 (1934).

[44] Blair, J. M., and Leighton, P. A., *J. Phys. Chem.,* **36,** 1649 (1932); *Phot. Korr. (Suppl.),* **69,** 27 (1933).

[45] See Berg, W. F., *Trans. Faraday Soc.,* **35,** 445 (1939); Berg, W. F., and Mendelssohn, K., *Proc. Roy. Soc. London,* **168A,** 168 (1938).

[46] Fesefeld, H., *Z. Physik,* **67,** 37 (1931).

[47] Frankenburger, W., and Fajans, K., *Z. physik. Chem.,* **105,** 255, 273 (1923). Pressure may prevent the formation of the latent image according to Poindexter, F. E., *J. Opt. Soc. Am.,* **21,** 59 (1931).

[48] Pauling, L., *Phys. Rev.,* **34,** 954 (1929).

a term representing the work done when an electron is brought into the crystal from an infinite distance. He believed this latter quantity a function of the diamagnetism of the crystal. It may be recalled that, in the case of the alkali halides, Hilsch and Pohl had used the ionization potential of the metal as the energy quantity to be deducted. They have also suggested that during the ripening of a photographic emulsion there may be produced centers analogous to the U centers of alkali halide crystals. Electrons in these centers could be lifted to the conductance zone by smaller quanta than those needed by electrons in the lower filled level. It appears likely that continued development of the newer quantum mechanical theories may serve to increase greatly our knowledge of the mechanisms involved.[49]

Mention must also be made of the observation that the sensitivity of a photographic emulsion is related to the presence in the grains of specks of a foreign substance.[50] Development of an exposed grain is known to start at these specks. These were at one time regarded as silver sulfide, serving the function of forming the anodes of minute photoelectric cells.[51] At present, they are thought to be due to the presence of organic sulfur compounds, derived from the gelatin of the emulsion.[52]

The more recent theories regard the function of the specks as that of concentrating the silver atoms liberated by the light. It may be that light absorbed at other portions of the grain moves through the grain as an "exciton" toward the disturbing speck.[53] A radically different theory, due to Stock,[54] denies the need for postulating sensitivity specks and regards the latent image as excited silver atoms on blocks of the grain, which is assumed to possess a mosaic structure.

Much effort has been expended in determining the properties which render a latent image developable. Toy and Edgerton [55] found the relative number of developable centers produced in silver bromide grains by exposure to monochromatic light to be proportional to the number of quanta absorbed by the silver bromide. Weigert [56] conceives of the latent image as complex micelles of silver halide, water, gelatin and "Ursilber" of increased energy content. This energy, which he believes may represent a summation of many quanta, is supposed to activate the developer molecules.

Trivelli [57] claims that the larger the specks originally present in an unexposed film, the smaller the amount of silver which needs to be added to it during exposure

[49] Gurney, R. W., and Mott, N. F., *Proc. Roy. Soc. London,* **164A,** 151 (1938); Berg, W. F., *Trans. Faraday Soc.,* **35,** 445 (1939); Berg, W. F., and Mendelssohn, K., *Proc. Roy. Soc. London,* **168A,** 168 (1938).

[50] Wightman, E. P., Trivelli, A. P. H., and Sheppard, S. E., *J. Frank. Inst.,* **194,** 485 (1922); Sheppard, S. E., and Wightman, E. P., *Ibid.,* **195,** 337 (1923); Sheppard, S. E., Wightman, E. P., and Trivelli, A. P. H., *Ibid.,* **196,** 653, 779 (1923); **198,** 507, 629 (1924); **200,** 335 (1925); Sheppard, S. E., Trivelli, A. P. H., and Loveland, R. P., *Ibid.,* **200,** 51 (1925); Clark, W., *Phot. J.,* **48,** 91 (1924); Toy, F. C., *Phil. Mag.,* **44,** 352 (1922); Sheppard, S. E., and Trivelli, A. P. H., *Phot. Korr.,* **64,** 145, 173, 242, 273 (1928); Svedberg, T., *Z. wiss. Phot.,* **20,** 36 (1920); *Chem. Abs.,* **15,** 2393 (1921); *Phot. J.,* **62,** 183, 186, 310 (1922).

[51] Trivelli, A. P. H., *J. Frank. Inst.,* **204,** 649 (1927); **205,** 111 (1928); *Phot. J.,* **68,** 67 (1928). *Contra,* Harrison, G. B., *Phot. J.,* **71,** *Sci. Tech. (Suppl.),* **1** (1931).

[52] Sheppard, S. E., *Phot. J.,* **49,** 380 (1925); *Nature,* **123,** 979 (1929); "Colloid Symposium Monograph," **3,** 76, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1925; Price, T. S., and Rawling, S. O., *Nature,* **116,** 281 (1925); Price, T. S., *Phot. J.,* **65,** 298 (1925); Silberstein, L., *Phil. Mag.,* **5,** 464 (1928).

[53] Compare Hecht, K., *Z. Physik,* **77,** 235 (1932).

[54] Stock, L. W., *Skrifter Norske Videnskaps-Akad. Oslo I, Mat.-natur. Klasse,* **No. 10,** 1-82 (1938); *Chem. Abs.,* **33,** 2827 (1939).

[55] Toy, F. C., and Edgerton, H. A., *Phil. Mag.,* **48,** 947 (1924).

[56] Weigert, F., *Z. wiss. Phot.,* **29,** 191 (1930); **30,** 217 (1931); *Chem. Abs.,* **25,** 1170 (1931); **26,** 3739 (1932); *Phot. Korr.,* **70,** *(Suppl.),* 41 (1934); *Naturwiss.,* **19,** 969 (1931).

[57] Trivelli, A. P. H., *Nature,* **126,** 760 (1930).

in order to produce a developable latent image. Sheppard [58] finds that the number of silver atoms produced by exposure and the preexisting nuclei are together too small to support the hypothesis of a minimum critical size for development centers. He believes the state and more particularly the orientation of the silver atoms is a more important determinant of the developability of nuclei than their size.[59] Reinders and Hamburger,[60] however, maintain that the smallest developable aggregates consist of three, four or more silver atoms or silver sulfide molecules.

The relation between the silver produced on development to the silver produced in the primary photoprocess is known as the development factor. It decreases with the grain size, being 3×10^8 for a grain mass of 6×10^{-12} and 10^3 for a grain mass of 10^{-16}. This is because the larger the grain, the greater the probability that it will contain a sensitizing nucleus of a certain size. Further details [61] of the theory of the sensitivity of photographic emulsions lie beyond the scope of this work.

Herschel Effect

In 1839, Sir John Herschel observed that red light causes a fading of the direct photochemical image produced by illuminating silver chloride. For a considerable time, this was regarded as an effect due to oxidation, but the observations of Leszynski [62] cast doubt on this, and, according to Trivelli,[63] more recent workers regard it as due to a photochemical bleaching of the latent image. Absorption of light by the latent image causes a photoconductivity, which tends to restore the original condition of the lattice by removing an electron from the silver atom and restoring it to the halogen. In the case of the alkali halides, the absorption of light by the latent image has two effects, the predominance of either of which is conditioned primarily by the nature of the crystal and its temperature. Bleaching predominates in the silver halides.[64] Lüppo-Cramer [65] has shown that the Herschel effect is not entirely confined to the red end of the spectrum, but may also occur when the intensity is small with yellow, green and even with blue light.

Sensitization

Sensitization to Longer Wave-Lengths. It has been observed that a silver bromide hydrosol containing adsorbed silver ion, in contrast to one with adsorbed bromide ion, shows increased absorption in the yellow and green regions. The absorption curve as a whole is shifted toward the longer wave-lengths by 150 to 200A, and at the same time the spectral sensitivity is shifted toward the longer wave-lengths.[66] Similar effects are also observed in gelatin emulsions. The thallous ion has a similar effect half as great.[67] To some extent the latent image

[58] Sheppard, S. E., *Phot. J.*, **71,** 313 (1931); *Chem. Abs.*, **25,** 5631 (1931).

[59] See also Arens, H., *Z. wiss. Phot.*, **30,** 49 (1931); Sheppard, S. E., *Ber. 8th Intern. Congr. Phot., Dresden,* **1931,** 13; *Chem. Abs.*, **27,** 237 (1933).

[60] Reinders, W., and Hamburger, L., *Z. wiss. Phot.*, **31,** 32, 265 (1932); *Chem. Abs.*, **26,** 4545 (1932); **27,** 2641 (1933).

[61] Fredenhagen, K., and Wellmann, M., *Z. physik. Chem., Bodenstein Festband,* 135 (1931); James, T. H., *J. Chem. Physics,* **2,** 132 (1934); Blair, J. M., and Hylan, M. C., *J. Opt. Soc. Am.*, **23,** 353 (1933); James T. H. and Coleman, J. J., *J. Chem. Phys.*, **2,** 483 (1934).

[62] Leszynski, W., *Z. wiss. Phot.*, **24,** 275 (1926); *Chem. Abs.*, **21,** 863 (1927).

[63] Trivelli, A. P. H., *J. Frank. Inst.*, **207,** 765 (1929).

[64] Smakula, A., *Z. Physik,* **59,** 603 (1929).

[65] Lüppo-Cramer, *Phot. Korr.*, **64,** 108 (1928).

[66] Fromherz, H., *Z. physik. Chem.*, **1B,** 324 (1928); Fajans, K., Fromherz, H., and Karagunis, G., *Z. Elektrochem.*, **33,** 548 (1927); Fajans, K., and Karagunis, G., *Naturwiss.*, **17,** 274 (1929); Fajans, K., and Steiner, W., *Z. physik. Chem.*, **125,** 275, 307 (1927).

[67] Fromherz, H., and Karagunis, G., *Z. physik. Chem.*, **1B,** 346 (1928).

itself may also act to sensitize a plate to longer wave-lengths.[68] These effects, however, are all of relatively little importance in comparison with the sensitizing effects which may be brought about by certain organic dyestuffs. These can be used to alter the natural sensitivity of photographic emulsions so as to render them either approximately equally sensitive to all of the visible wave-lengths or to extend the range of sensitivity into the infrared or to the shorter ultraviolet regions.

In 1873, Vogel noticed that certain dyes, such as Corallin, which has an absorption band in the yellow-green, sensitized plates to the region which these dyes absorb. The Isochromatic plates of fifty years ago, sensitized with eosin, were the first color-sensitive plates to have been generally used. Many other dyes have since been found more satisfactory. Particularly important are the isocyanine dyes, as ethyl red, carbocyanines, including pinacyanol, and a number of others as kryptocyanine and neocyanine. The use of such dyes has made possible the advances in long-range, haze-penetrating, infrared photography.

The theory underlying the action of these dyes is still somewhat obscure. The range of sensitization and the absorption spectra of the dyes do not coincide as closely as had been at first thought to be the case. It has, however, been suggested that the dyes when adsorbed on the halide grains may have their absorption spectra shifted.[69] In some instances obscure chain reactions may be set up. Not all dyes sensitize when adsorbed. A common constitutional factor in the effective ones appears to be the existence of either two oxygen or two nitrogen atoms in two states of valency, joined by a chain of conjugated double bonds.[70]

Rabinovich has suggested that in solid systems the energy evolved in the photoöxidation of the adsorbed sensitizer by atmospheric oxygen may be utilized in the decomposition of the crystals to which it is adsorbed.

Ultraviolet Plates. Duclaux and Jeantet [71] suggested that a photographic plate may be sensitized to the extreme ultraviolet by the application of a thin coating of oil. Lyman [72] believes the process does not yield results comparable with the Schumann procedure (Chapter 1), but agrees that its possibilities have not been fully explored. The changes in sensitivity and contrast produced by coating plates of various brands with five different fluorescent oils, in the region of 2200-3800A have been studied by Harrison [73] and by Söderman,[74] the latter finding only Schumann plates to be satisfactory in the range 50-500A. A 0.5 per cent solution of vaseline in light petroleum may be employed.[75] Citric acid and salicylates have also been used.[76] Eggert and Arens [77] have added to ordinary

[68] Eggert, J., and Noddack, W., *Z. Physik,* **31,** 942 (1925). *Synthetic Organic Chemicals, Eastman Kodak Co.*, Dec. 1927. For the earlier observations, including those of Becquerel, Lüppo-Cramer and of Fajans, see Mees, C. E. K., *J. Frank. Inst.*, **201,** 525 (1926).

[69] See also Rabinovich, A. J., *Sci. ind. Phot.*, **6,** 288 (1935); *Chem. Abs.*, **30,** 3343 (1936).

[70] For further studies of the sensitizing action of erythrosine on colloidal solutions of silver bromide, see Bokinik, Y. I., and Il'ina, Z. A., *Acta Physicochim. U.R.S.S.*, **3,** 383 (1935). *Chem. Abs.*, **30,** 3297 (1936). For the recent development of sensitization theories, Wahl, H., *Chim. et Ind.*, **36,** 16 (1936); Rabinovich, A. J., *Acta Physicochim. U.R.S.S.*, **3,** 368 (1935); *Chem. Abs.*, **30,** 3343 (1936); Webb, J. H., *J. Opt. Soc. Am.*, **26,** 367 (1936); Bokinik, Y. A., and Il'ina-Bagdasar'yan, Z. A., *J. Phys. Chem. U.R.S.S.*, **11,** 197 (1938); *Chem. Abs.*, **33,** 3277 (1939); Bagdasar'yan, K. S., *Acta Physicochim. U.R.S.S.*, **9,** 205 (1938); *Chem. Abs.*, **33,** 5759 (1939); Sheppard, S. E., Lambert, R. H., and Walker, R. D., *J. Chem. Phys.*, **7,** 426 (1939).

[71] Duclaux, J., and Jeantet, P., *Science,* **58,** 48 (1923); *J. phys. radium,* **2,** 156 (1921); *Chem. Abs.*, **15,** 2798 (1921).

[72] Lyman, T., *J. Frank. Inst.*, 5560, May, **1926.**

[73] Harrison, G. R., *J. Opt. Soc. Am.*, **11,** 113 (1925).

[74] Söderman, M., *Z. Physik,* **67,** 790 (1931).

[75] Beach, A. C. G., *Nature,* **123,** 166 (1929).

[76] J. and J. F. Thovert, *Bull. seances soc. franç. phys.*, **1932,** 158; *Chem. Abs.*, **27,** 5662 (1933).

[77] Eggert, J., and Arens, H., German P. 640,157, Dec. 23, 1936. (To I. G. Farbenindustrie); *Chem. Abs.*, **31,** 2112 (1937).

plates a layer containing a wetting agent and a substance such as fluorene or anthracene which fluoresces in the ultraviolet region. The purpose of the wetting agent, saponin or Turkey-red oil, is to aid in the removal of the fluorescent substance in the development bath. Rathenau [78] suggests impregnating the plate with a filtering dye which absorbs light of fairly long wave-length and then covering it with a sensitizing oil film which acts on short wave-lengths unabsorbed by the dye. Among the dyes proposed were nitrosodimethylamine, methyl orange, fuchsine. As the sensitizer, Cenco pump oil 11021B could be used.

Details of the sodium salicylate method, including the sensitometry of the plates so treated, have been given by Montagne and Ricard,[79] Kiu,[80] and Terrien.[81]

Ethyl dihydrocollidinedicarboxylate has been proposed.[82] Sheppard and Vanselow [83] use a silver salt of 1-*p*-sulfophenyl-3-methyl-5-pyrazolone, or related compounds. A number of solutions enumerated by Allen and Franklin [84] for sensitizing plates to radiations shorter than 2500A are shown in Table 20. The aqueous

Table 20. Substances Used for Ultraviolet Sensitization of Plates.

	Chemical Name	Trade Name	Solvent	Approximate Concentration	Remarks
1.	1-naphthylamine-4-sulfonic acid	Naphthionic Acid	Water	2%	Add 4% Na_2CO_3
2.	2-naphthylamin-1-sulfonic acid	Eastman's T386	"	2%	"
3.	2-naphthylamine-6-sulfonic acid	Bronner's Acid	"	2% (sat)	"
4.	2-naphthylamine-6,8-disulfonic acid	Amino G Acid	"	4%	"
5.	2-naphthol-6,8-disulfonic acid	G Acid	"	4%	"
6.	α-naphthylamine		Ethyl acetate	2%	Add 4cc. alcoholic solution of white shellac per 100 cc.
7.	Fluorene		"	2.5%	"
8.	Carbazole		"	2%	"
9.	Ethyl carbazole		"	2%	"

solutions are merely applied to the plates for a few seconds, after which the plates are allowed to dry in a vertical position. Just before development, the plates should be rinsed with water. When water-insoluble organic substances are used, these should be removed before development by means of acetone. The same treatment should be used on plates treated with fluorescent oils or Eastman sensitizer.

In a photosensitive layer sensitive to the ultraviolet, Sheppard and Eberlin [85] use for application to paper dextrose and an oxygen-containing compound of a metal of the sixth periodic group having an atomic weight between 90 and 200, such as sodium tungstate or molybdate.

[78] Rathenau, G., *Physica,* **2,** 840 (1935).

[79] Montagne, R., and Ricard, R., *Compt. rend.,* **202,** 477 (1936).

[80] Kiu, T., *Compt. rend.,* **201,** 1348 (1935); *Sci. ind. phot.,* **8,** 1 (1937); *Chem. Abs.,* **31,** 2948 (1937).

[81] Terrien, J., *Compt. rend.,* **202,** 211 (1936).

[82] Burroughs, R. E., U. S. P. 1,880,411, Oct. 4, 1933. (To Eastman Kodak Co.). *Chem. Abs.,* **27,** 675 (1933).

[83] Sheppard, S. E., and Vanselow, W., U. S. P. 2,066,582 (To Eastman Kodak Co.), *Chem. Abs.,* **31,** 962 (1937).

[84] Allen, A. J., and Franklin, R. G., *J. Opt. Soc. Am.,* **22,** 469 (1932).

[85] Sheppard, S. E., and Eberlin, L. W., U. S. P. 1,934,451, Nov. 7, 1934 (To Eastman Kodak Co.); *Chem. Abs.,* **28,** 426 (1934).

Russell Effect. It has long been known that a very great number of substances are capable of affecting a photographic plate in the dark (Russell effect). An exhaustive review of the work in this field has been given by Keenan,[86] who concludes that, in general, a vapor passes from the active substance to the plate, and that it is of the nature of hydrogen peroxide or an organic peroxide.

The Weigert Effect

It was shown by Weigert [87] that exposure of very thin layers of silver chloride (when sensitized by free silver produced by a previous exposure to ordinary light) to plane polarized light renders the layer color-adapted and dichroic, that is, causes it to exhibit different extinction coefficients in polarized light according to the direction of the plane of polarization. This is a sign of a definite anisotropy in the layer. The optical axis of the photoanisotropic system is always parallel to the plane of the electric vector. After a preliminary exposure to polarized light, the orientation set up determines or orients a subsequent decomposition effected by non-polarized light. This Weigert termed induced photoanisotropy. Zocher and Coper [88] have obtained the effect by the use of circularly polarized light. Weigert regarded the effect as due to definite alterations in the shape of complex silver micelles. It has, however, been shown by Cameron and Taylor [89] that the effect can be produced in single crystals of silver chloride previously rendered blue by exposure. Both silver and a silver halide lattice are necessary, but gelatin or other components of photographic emulsions or the gel state are not essential. It is suggested that suitably dimensioned and oriented silver particles can respond to polarized light by ejecting electrons in a definite direction. These reform silver from the silver ions in the lattice, the chlorine being assumed to migrate.

Weigert also observed the phenomenon in the photodecomposition of light-sensitive dyes embedded in gelatin.[90] In cases in which there is rigidity, either of a crystal lattice or of a gel, photoanisotropy effected by polarized light may persist. In gaseous or liquid systems, in which the photochemical products are rapidly disoriented by collisions, it is evanescent.[91]

Other Silver Compounds

Wave-lengths longer than 2500A are said not to reduce silver nitrate in pure gelatin, unless there is present 10^{-5} gram mole of potassium chloride or bromide per liter of gelatin. Even eosin or rhodamine-silver nitrate-mannitol mixtures are stable in ultraviolet light if they have previously been subjected to ultrafiltration.[92]

[86] Keenan, G. L., *Chem. Rev.,* **3,** 95 **(1926).**

[87] Weigert, F., *Verhand. deut. physik. Ges.,* **21,** 479 (1919); summarizing statements in *Naturwiss.,* **9,** 583 (1921); **16,** 613 (1928); **19,** 969 (1931); *Z. physik. Chem.,* **3B,** 377 (1929); **4B,** 239, 258 (1929); **18B,** 73 (1932); see also Nikitine, S., *Compt. rend.,* **204,** 973 (1937); **208,** 513, 643 (1939); Cherduintzev, S., *Acta Physicochim. U.R.S.S.,* **3,** 355 (1935); *Chem. Abs.,* **30,** 2110 (1936); Ungar, G., *Compt. rend.,* **208,** 337 (1939).

[88] Zocher, H., and Coper, K., *Z. physik. Chem.,* **141,** 217 (1929); **132,** 313 (1928). See also Cotton, A., *Compt. rend.,* **189,** 599 (1929).

[89] Cameron, A. E., and Taylor, A. M., *J. Opt. Soc. Am.,* **24,** 316 (1934).

[90] See also Nikitine, S., *Compt. rend.,* **208,** 805 (1939).

[91] Ghosh, J. C., and Banerjee, T., [*Kolloid-Z.,* **86,** 372 (1939)] have recently reviewed extensive experiments on the production of circular dichroism in various inorganic sols by irradiation with circularly polarized light during their formation.

[92] Bokinik, Y. A., *J. Phys. Chem. (U.S.S.R.),* **11,** 190 (1938); *Chem. Abs.,* **33,** 4130 (1939).

A solution containing starch, silver nitrate and an excess of potassium iodide rapidly becomes blue on exposure to light. Since the reaction is not observed in the presence of an excess of the silver ion, it may be assumed that the iodine liberated is derived from potassium iodide adsorbed on silver iodide, the latter exerting an enormous accelerating influence on the oxidation of the former.[93]

According to Ishii,[94] the compound $AgKI.2H_2O$ exists as asbestos-like crystals which change from peach color to dark purple under sunlight and to dark gray under mercury arc light. Rather similar changes are also observed in the colorless compounds $2AgI.KI.1/2H_2O$ and $2AgI.KI.2H_2O$. The compound $4AgI.KI.2C_3H_6O$ is not affected by sunlight but changes from colorless to a peach color under the mercury arc. Ag.2KI and Ag.6KI are unaffected by light.

Arens and Eggert[95] found sensitive gelatin emulsions of silver acetylide, azide or oxalate to be developable under suitable conditions. Each of the three salts is white and absorbs in the same region of the ultraviolet as does silver chloride. After a long exposure of the acetylide, a residue of carbon is found on dissolving away the silver. Nitrogen separates directly from the azide on exposure to light of high intensity, but this does not occur as a result of a correspondingly longer exposure to light of a lower intensity. Possibly in this case hydrogen azide is formed. Contrary to what might be expected from their endothermic nature, the amount of silver which separates directly on exposure of either of these three salts is of the same order of magnitude as that formed from silver chloride.

There are photographic processes which do not employ silver salts. Among these are the bleaching of photosensitive dyes, generally by oxidation, diazo-processes in which after the loss of nitrogen the remaining residue of the diazo-body can be coupled to form a dye, alkaline bichromate processes in which there forms a chromic oxide capable of tanning gelatin and certain iron processes.

Gelatin impregnated with ferric chloride gives a white image when exposed under a negative.[96] Mixtures of tartaric acid and ferric salts with selenious acid or with potassium tellurate are reduced in light with the formation of amorphous selenium or tellurium. Sensitive papers utilizing this behavior have been prepared.[97] The selenium paper gives a bright red and the tellurium paper a black to brown tone. The development and fixation may be carried out with a dilute solution of hydrochloric acid, with the addition, in the case of the tellurium paper, of stannous chloride to prevent the destruction of the image by the unchanged ferric chloride.

The Blackening of Lithopones

The white pigment lithopone, a mixture of zinc sulfide and barium sulfate, is prone to blacken on exposure to ultraviolet radiations from an arc or in sunlight. Eibner[98] attributed this to an interaction of metallic impurities with the sulfide pigment. Roches[99] attached much importance to the presence of chlorides, but

[93] Hiller, W., *Z. anorg. Chem.*, **219**, 313 (1934); *Brit. Chem. Abs.*, **1934A**, 1183.

[94] Ishii, S., *Repts. Osaka Imp. Ind. Research Inst. Japan*, **11**, No. 20 (1931); *Chem. Abs.*, **25**, 5362 (1931).

[95] Arens, H., and Eggert, J., *Phot. Korr.*, **67**, **No. 8**, 17 (1931); *Veröffentl. wiss. Zentral-Lab. Phot. Abt.* AGFA **3**, 67 (1933); *Chem. Abs.*, **26**, 1529 (1932); **28**, 3012 (1934); Moskovich, S. M., *J. Phys. Chem* (*U.S.S.R.*), **12**, 460 (1938); *Chem. Abs.*, **33**, 4892 (1939).

[96] Schommer, F., *Atelier Phot.*, **33**, 91 (1926); *Chem. Abs.*, **21**, 538 (1927).

[97] Pavolini, T., *Giorn. Chim. Ind. Appl.*, **12**, 72 (1930); *J. Soc. Chem. Ind.*, **1930**, Suppl. 533.

[98] Eibner, A., *Chem. Ztg.*, **49**, 345, 370 (1925). The darkening of red mercuric sulfide was also discussed.

[99] Roches, C., *Rev. chim. ind.*, **31**, 109 (1922); *Chem. Abs.*, **16**, 3217 (1922). See also Schleede, A., Herter, M., and Kordatzki, W., *Z. physik. Chem.*, **106**, 386 (1923).

did not find iron, cadmium, cobalt or manganese harmful. Brickwedde[100] believed soluble salts whose sulfides are black to promote the change. The elimination of impurities from the raw materials employed in the manufacture of this pigment has greatly increased its light stability.[101] It is, nevertheless, true that even carefully purified Wurtzite, zinc blende and unignited zinc sulfide, in the presence of water, blacken when subjected to ultraviolet rays.[102] In an atmosphere of hydrogen, the decomposition products contain hydrogen, zinc, sulfur, and the zinc and sulfate ions. Electrolytes increase the light-sensitivity. By irradiating a suspension of zinc sulfide in water, Job and Emschwiller[103] had previously obtained sulfur, zinc and hydrogen.

It was believed by Mass and Kempf[104] that the lattice structure is essential to the blackening and that amorphous freshly precipitated zinc sulfide or zinc sulfide which has been ground in a mortar is insensitive to light. Such samples must be subjected to heat treatment to convert them into phosphors before they will blacken.[105] Only luminescent samples exhibit the phenomenon, possibly because neutral atoms of zinc, cadmium or silver must be present in the interstices of the lattice.[106] Mass and Kempf attributed the change in the zinc sulfide to a process analogous to that which occurs during the exposure of silver bromide; zinc and zinc disulfide were assumed to be formed, the zinc appearing in finely divided form on the surface of the mass. It may be that in the primary process, electrons pass from a sulfide ion on the surface of the crystal lattice and discharge a neighboring zinc ion. Irradiation produces photoconductivity, but there are differences in the spectral sensitivity curves for blackening and for photoconductivity. Gordon, Seitz and Quinlan[107] have speculated regarding the nature of the two-quantum shifts of electronic energy-levels involved. They believe the blackening occurs at the surface as an electrolysis of zinc sulfide in solution in the surface moisture under the electromotive force produced by the optically-formed Zn^+ and S^- ions. The liberation of hydrogen noted by Job and Emschwiller has not yet been interpreted in terms of the newer theories.

Glycerol and other polyatomic alcohols have been believed to protect lithopones.[108] Waterglass is also said to be effective.

It was observed by Mass and Kempf that blackened lithopone brightens in darkness owing to the oxidation of metallic zinc, but remains black if no oxygen is present. The rate of bleaching of darkened lithopone and the photoelectric effect of the latter are similar to the behavior of samples of lithopone upon the surface of which zinc has been distilled.[109]

To determine the relative effectiveness of various wave-lengths, Pfund[110]

[100] Brickwedde, F. G., *J. Opt. Soc. Am.*, **14**, 312 (1927).

[101] Eibner, A., *Farben Ztg.*, **30**, 2600 (1925); *Chem. Abs.*, **19**, 3601 (1925).

[102] Platz, H., and Schenck, P. W., *Z. angew. Chem.*, **49**, 822 (1936).

[103] Job, A., and Emschwiller, G., *Compt. rend.*, **177**, 313 (1923); see also Weiser, H. B., and Garrison, A. D., *J. Phys. Chem.*, **31**, 1237 (1927).

[104] Mass, E., and Kempf, R., *Z. angew. Chem.*, **36**, 293 (1923); *J. Chem. Soc.*, **124**, ii, 491 (1923).

[105] See, however, Streck, E., *Ann. Physik*, **34**, 96 (1939); **35**, 58 (1939).

[106] Seitz, F., *J. Chem. Phys.*, **6**, 454 (1938); Brusilowskii, A. M., Sigal, F. S., and Kabanova, E. Y., *Lakokrosochnuyu Za*, **1935**, No. 3, 11; *Chem. Abs.*, **31**, 6485 (1937); Brusilowskii, A. M., *Org. Chem. Ind. (U.S.S.R.)*, **5**, 493 (1938); *Chem. Abs.*, **33**, 883 (1939).

[107] Gordon, N. T., Seitz, F., and Quinlan, F., *J. Chem. Phys.*, **7**, 4 (1939); compare Stobbe, H., *Z. wiss. Phot.*, **29**, 209 (1930); *Chem. Abs.*, **25**, 1441 (1931).

[108] Nishizawa, Y., *J. Tokyo Chem. Soc.*, **41**, 1054 (1920); *Chem. Abs.*, **15**, 1407 (1921); see also, British P. 156,971, Nov. 25, 1919; Gardner, H. A., and Holdt, P. C., *Paint Mfrs. Assn. Circ.*, **194**, 174 (1924); *Chem. Abs.*, **18**, 910 (1924).

[109] Brickwedde, F. G., *J. Opt. Soc. Am.*, **14**, 312 (1927). See also Goshorn, J. C., and Black, C. K., *Ind. Eng. Chem.*, **21**, 348 (1929).

[110] Pfund, A. H., *Proc. Am. Soc. Testing Materials*, **23**, II, 375 (1923).

rubbed a sample in water and covered it with a quartz plate. The specimen was then mounted in the focal plane of a quartz spectrograph, so that the entire spectrum from an iron arc was projected upon the lithopone surface, which, by darkening indicated the spectral regions of greatest effectiveness. Wave-lengths longer than 3200A showed very little darkening. By the use of monochromatic light of constant intensities, it was shown that the sensitivity of lithopone is almost nil in the visible spectrum, and rises to a high value in the ultraviolet near 2900A, remaining practically constant at shorter wave-lengths. All samples of lithopones tested by Pfund showed the same general type of sensitivity curves. These curves were obtained by plotting against the wave-lengths the reciprocals of the time in seconds required to produce a visible darkening by these wave-lengths, the intensity being maintained constant. Brickwedde, employing this method, found very different results, the sensitivity beginnig at 3700A and showing a subsidiary maximum at 3130A.

In testing lithopones, Gardner and Holdt[111] use either an exposure to sunlight, or as an accelerated test, to the rays of a mercury or iron arc. When the mercury arc is used, the pigment is exposed as a dried oil paint film on a palette submerged in a shallow layer of water to reproduce a condition of constant humidity. The test should be carried out on the pigment ground in the vehicle in which it is intended to be used. The acid value of the oil medium used has a marked effect, increasing acid values in a series of alkali-refined linseed and tung oils diminishing but not entirely inhibiting the darkening of the pigment. When employing the rays from an iron arc, the lithopone paste is exposed behind a quartz slide, backed by an ordinary glass slide to retard evaporation. When sunlight is used, ordinary thin microscope slides may be used. The degree of darkening may be evaluated by comparison with standards.

Some reversible darkening in daylight of commercial samples of titanium oxide,[112] particularly in those containing iron, has been observed to occur. Vermillion is also light-sensitive.[113]

Effect of Ultraviolet Radiations on Colloidal Systems

Preparation. Although Schulze[114] was unable to effect the conversion of metals into dusts by the action of ultraviolet radiation, Svedberg[115] succeeded in preparing colloidal sols of metals by applying an observation of Lenard and Wolf[116] that certain substances, especially metals, are disintegrated when exposed to ultraviolet rays. Pieces of metal, the surfaces of which had been carefully freed from oxides, were placed in a shallow dish containing a dispersion medium, and exposed to the rays from a Heraeus quartz mercury arc lamp at a distance of a few centimeters. After a few minutes, colloidal sols were obtained from silver, copper, tin and lead, but platinum, aluminum and cadmium remained practically unaffected. The action was especially marked in the case of lead, which yielded a colloidal sol in ethyl alcohol, and a milky liquid, probably containing lead hydroxide, in water. The nature of the dispersion medium had a great influence on the results with silver and lead. Kimura[117] tested the effect of ultraviolet rays on silver, copper

[111] Gardner, H. A., and Holdt, P. C., *U. S. Paint Mfrs. Circ.*, **194**, 174 (1924); *Chem. Abs.*, **18**, 910 (1924).
[112] Williamson, W. O., *Nature*, **140**, 238 (1937); **143**, 279 (1939).
[113] Six, G., and Bover, J. R., *Paint Manuf.*, **8**, 367 (1938); *Chem. Abs.*, **33**, 883 (1939).
[114] Schulze, F., *Ber. Physik. Ges.*, **1912**, 246; *Chem. Abs.*, **6**, 1708 (1912).
[115] Svedberg, T., *Ber.*, **42**, 4375 (1909); *Z. Chem. Ind. Colloide*, **6**, 129, 238 (1910).
[116] Lenard and Wolf., *Ann. Phys. Chim.*, **37**, 443 (1889).
[117] Kimura, M., *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, **5**, 253 (1913); *Chem. Abs.*, **8**, 611 (1914).

and an alloy of cadmium 90 per cent and antimony 10 per cent. In a vacuum, no corrosion took place, in air, there was a very slight corrosion, in oxygen somewhat more and in water strong corrosion under the influence of the rays. Nordenson,[118] who continued these experiments, using quantitative methods, ascribed the formation of the colloidal sols by the rays to the formation of hydrogen peroxide. This attacks the metal, yielding an oxide or hydrate which after solution is converted to a metallic colloid by the reducing action of the rays.

Dede and Walther[119] obtained yellow to bluish-violet colloidal solutions of arsenic by bubbling purified arsine through water exposed to light of short wave-lengths.

Voigt[120] has stated that pure silver nitrate in very dilute solution does not form a silver hydrosol when exposed to the rays from a quartz lamp except in the presence of a protective colloid such as gum arabic. The wave-length is important, ultraviolet rays being required. The ultramicroscopic particles of the gum act as reducing centers.

Wassiljewa[121] notes that if dilute hydrochloric acid is added to a solution of sodium tungstate until the liquid becomes slightly acid, a colloidal solution of tungstic acid is obtained. This, in the presence of various organic substances such as formaldehyde, sucrose, dextrose or dextrin, undergoes reduction on exposure to light, with the formation of an intensely blue solution. If the undialyzed solution is kept for some time, it is found that the reduction process does not occur when the solution is exposed to light. This may be due to the existence of two forms of colloidal tungstic acid, one of which is photochemically inert and the other sensitive to light. The latter changes spontaneously into the former. The reverse transformation may be brought about by a rise of temperature. The absorption spectra of the two modifications are found to differ appreciably, the region of ultraviolet absorption extending further towards the visible spectrum in the case of the photochemically sensitive modification. Ghosh and Bhattacharya[122] found that it takes three minutes to start the photochemical reduction of tungstic acid by glucose in the presence of sunlight. The rate of reaction then increases up to eight minutes, after which it obeys a zero-molecular law. This period of induction is probably due to the fact that the aggregated molecules must first be broken up into simple molecules before the reduction begins.

It has been claimed[123] that alumina intended for use as an emulsifying agent in the manufacture of cosmetics, paints and cleaning agents may be improved by ripening it by ultraviolet irradiation.

In determinations of particle size in colloidal sols, it has been possible to make observations of the Tyndall cone produced by ultraviolet as well as by visible light.[124, 125]

Effects of Irradiation on the Stability of Colloidal Systems. Ultraviolet rays cause a slight decrease in the electrophoretic migration velocity of zinc hydro-

[118] Nordenson, H., *Kolloidchem. Beihefte*, **7**, 110 (1915).
[119] Dede, L., and Walther, T., *Ber.*, **58B**, 99 (1925). For data on the effects of ultraviolet irradiation upon the growth of the particles of sulfur and of gum mastic sols, see Audubert, R., *Ann. Phys.*, **18**, 5 (1922); *Chem. Abs.*, **16**, 3812 (1922).
[120] Voigt, J., *Kolloid-Z.*, **43**, 30 (1927); **45**, 319 (1928).
[121] Wassiljewa, A., *Z. wiss. Phot.*, **12**, 1 (1913); *J. Chem. Soc.*, **104**, ii, 265 (1913).
[122] Ghosh, S., and Bhattacharya, A. K., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 29 (1932); *Chem. Abs.*, **27**, 2097 (1933); Ghosh, J. C., and Banerjee, T., *Kolloid-Z.*, **86**, 372 (1939).
[123] Dickerson, T. W., British P. 487,855, June 25, 1938.
[124] Lohfert, H., *Kolloid-Z.*, **51**, 65 (1930).
[125] With reference to the action of ultraviolet in producing fog nuclei, see Ramsauer, C., *Ber. deut. Physik. Ges.*, **13**, 899 (1911); *J. Chem. Soc.*, **102**, ii, 5 (1912). On the formation of nuclei in moist air, Saltmarsh, M., *Proc. Phys. Soc.*, **27**, 357 (1915).

sols, but not alcosols, according to Schaum and Friederich.[126] Light also affects the electrophoresis of silver halide hydrosols and may even reverse the direction of migration of the particles. The migrations of many other sols were not, however, affected by light in Schaum's experiments.

A number of investigators have studied the effect of ultraviolet light in altering the stability of particle size of previously prepared colloidal sols. In experiments in which silver sols prepared by the high-frequency arc method were adsorbed by filter paper and exposed to the rays, Long[127] found the more highly dispersed ones to be particularly sensitive. Wiegel[128] also noted that coagulation of dextrin-silver sols is accelerated by light, and especially the shorter wave-lengths. Galecki and Spychalski[129] found that the smaller the particles of silver nuclear hydrosols, the more readily were they decolorized by ultraviolet rays. The conductivity increases and the viscosity decreases, but these changes may be reversed on prolonged irradiation. It is suggested that the radiation causes the formation of hydrogen peroxide, which dissolves the colloidal silver and decolorizes the sol by forming silver ion. This may subsequently be reduced by the action of the ultraviolet rays. The reaction, as followed by spectrophotometry at 5100A, appeared to be of the first order. The values of the reaction velocity constants varied at 10° from 0.0528 to 0.1345 and at 29° from 0.0875 to 0.2104 for the particular sols used. The temperature coefficient had a mean value of 1.3. According to Galecki and Marchlewska,[130] gelatin and ageing increase the time required for ultraviolet light to decolorize the sols.

The coagulation of Bredig's platinum hydrosol[131] may be greatly hastened by exposure to a 220-volt Cooper-Hewitt quartz lamp at a distance of 15 cm. A platinum sol which was not completely coagulated in two years in ordinary light was half coagulated in ten hours of irradiation. Similarly, the rays accelerate the coagulating action of common salt.

Zakowski[132] finds the induction period or period of slow growth of gold particles upon gold nuclei to be diminished by previous irradiation of the gold solution by ultraviolet light. Beaver and Muller[133] have reviewed the many older observations regarding the effect of light in reducing gold salts or in accelerating the action of reducing agents in the formation of colloidal gold. Nordenson[134] was convinced that the coagulating effect of the ultraviolet rays upon gold sols was not due to a photoelectric effect because the result was the same for positively and for negatively charged particles. He suggested either that the light may cause a difference of potential between adjacent particles leading to attraction and eventual precipitation, or that the light may disturb the adsorption equilibrium between particles and associated ions, leading to instability and coagulation. Beaver and Muller attempted to determine why the sensitivity of gold sols is markedly dependent upon their past history, some being entirely unaffected by ultraviolet light, while others are readily coagulated by it. Fourteen days' exposure to a 220-volt mercury arc did not affect Bredig gold sols or sols prepared by

[126] Schaum, K., and Friederich, P., *Z. wiss. Phot.*, **23**, 98 (1924); *Chem. Abs.*, **19**, 1376 (1925).
[127] Long, S. H., *Kolloid-Z.*, **14**, 136 (1914).
[128] Wiegel, E., *Z. wiss. Phot.*, **24**, 316 (1927); *Brit. Chem. Abs.*, **A1927**, 411.
[129] Galecki, A., and Spychalski, R., *Roczniki Chem.*, **8**, 394 (1928); *Z. anorg. allgem. Chem.*, **177**, 337 (1928); *Kolloid-Z.*, **53**, 338 (1930); *Chem. Abs.*, **23**, 1572 (1929); **25**, 876 (1931).
[130] Galecki, A., and Marchlewska, J., *Kolloid-Z.*, **59**, 206 (1932).
[131] Spear, E. B., Jones, P. F., Neave, A. S., and Schlager, M., *J. Am. Chem. Soc.*, **43**, 1385 (1921).
[132] Zakowski, J., *Kolloidchem. Beihefte*, **23**, 117 (1926).
[133] Beaver, J. J., and Muller, R. H., *J. Am. Chem. Soc.*, **50**, 304 (1928).
[134] Nordenson, H., *Z. physik. Chem.*, **90**, 603 (1915).

means of hydrazine, phosphorus, formaldehyde or acetylene. On the other hand, sols prepared by means of hydrogen peroxide, tannin, quinol, catechol, resorcinol or pyrogallol, turned blue within the first two days, the light having a slow coagulating effect. After eight days of irradiation, they turned clear red, the unstable sol being peptized to a sol identical in appearance and behavior with the one originally used. After this, light had no further effect. In the case of the tannin and hydrogen peroxide sols, the stability toward ultraviolet radiation was in general dependent upon the pH at which the reduction had originally been brought about. The sensitivity toward radiation was progressively less as neutrality was approached, and was at a minimum at slight alkalinity for the peroxide sols. In the range of pH 7.5 to 9.0, the sensitivity, although slight, varied, so that a number of the sols identical in appearance exhibited different behavior toward the light. Radiation of wave-lengths shorter than the 2150A line is required for the change from red to blue. In a tannin sol, there was a slight but definite increase of the refractive index as the sol became blue. It decreased again as the sol was peptized by the radiation. The changes were even less in a hydrogen peroxide sol. The conductivity changed in a similar manner to the extent of about 0.3 per cent. These effects were attributed to changes in the amounts of stabilizing ions adsorbed. As more ions appeared in the solution in the first part of the irradiation, fewer were adsorbed and the stability was decreased. The absorption spectrum of the sol proved one of the most sensitive indicators of the changes taking place. Conductance titrations with silver nitrate indicated an increased concentration of chloride ion in the bulk of the solution in the blue sol and a return to the original concentration in the peptized red sol. Although the original and the red final states appeared to be identical, it was evident from the photochemical indifference of the latter that they are in fact different. This was also apparent from spectrograms in the far ultraviolet, since the peptized sol no longer absorbed the effective radiation. It is possible that when peptization had been effected, the ions were more firmly associated with the complex; this would account for the greater stability toward light as well as for the lack of absorption bands in the effective region.[135]

It has been shown by Murphy and Mathews[136] that the electrical conductivity of arsenic trisulfide hydrosol increases upon exposure to light, the rate of change increasing somewhat with decreasing concentration of the colloid.

According to Freundlich and Moor,[137] a mixture of silver and arsenious sulfide sols undergoes in the dark a change of color from a golden-brown through greenish-brown to lilac, and, with exposure to light, through green to a golden-brown. Both changes are prevented in the presence of a gelatin gel. The reaction in the dark is regarded as a direct interaction between the particles of the two sols. The secondary change under the action of light is purely chemical and involves oxygen and the probable formation of a silver thioarsenite. Horiba and Baba[138] find that on illumination, arsenious sulfide and Congo red sols, but not ferric or chromic hydroxide sols, exhibit increased osmotic pressure. Colloidal cuprous hydroxide, formed by boiling cuprous chloride or bromide with aqueous gelatin, is photosensitive in the presence of acid.[139]

The reactions of gold and silver sols with arsenic and antimony trisulfide sols

[135] See also Thiessen, P. A., *Kolloidchem. Beihefte*, **29**, 122 (1929).
[136] Murphy, R. V., and Mathews, J. H., *J. Am. Chem. Soc.*, **45**, 16 (1923).
[137] Freundlich, H., and Moor, F., *Kolloid-Z.*, **36**, 17 (1921).
[138] Horiba, S., and Baba, H., *J. Phys. Chem. Japan*, **3**, 1 (1929); *Brit. Chem. Abs.*, **A1930**, 691.
[139] Horiba, S., and Ishii, S., *J. Phys. Chem. Japan*, **2**, 118 (1929); *Brit. Chem. Abs.*, **A1930**, 691.

are photosensitive.[140] Rapid color change is produced by sunlight and the product is found to consist of metallic sulfides, free sulfur and arsenious or antimonious acids.

Krestinskaya[141] found arsenious sulfide sols to be rendered more stable toward the barium ion by exposure to light. Sols of different concentrations and compositions were, however, affected differently in respect to the coagulating action of other ions. According to Joshi, Barve and Desai,[142] on exposure of an arsenious sulfide sol to light, the charge on the particles decreases, the conductivity increases, the total sulfur decreases, the stability to potassium chloride passes through a maximum, and the stability to magnesium chloride decreases continuously. These effects are attributed to the hydrolysis of the sulfide to arsenious acid and hydrogen sulfide, the latter yielding sulfur dioxide, sulfur and pentathionic acid.

Boutaric and Bouchard[143] found the time of coagulation of arsenious sulfide and other sols by electrolytes in the presence of fluorescein, eosin or erythrosin, was in all cases decreased by illumination, the effect being greater in ultraviolet than in visible light freed from infrared. Potassium sulfate and sulfuric acid, which inhibit the fluorescence of the dyes, also suppress the effect of the light. The light had no effect in the absence of the fluorescent compounds, and the dyes did not affect the sols in the dark. The difference between the time required for flocculation in the dark and in daylight or ultraviolet light is proportional to the logarithm of the fluorescing power of the mixture of fluorescein and added electrolyte, if any. Tannin, hydroquinone, phenol and cresol in the presence of lithium chloride also reduce both the fluorescing power and the shortening of the flocculation time. Eosin and erythrosin which have absorption bands close to that of fluorescein, reduce its fluorescence and also reduce its effect on the flocculation time. The difference in the time required for flocculation in the dark and in ultraviolet light is reduced from 60 to 15 minutes by 0.05 per cent Direct-Scarlet solution. A number of colorless substances which fluoresce in the ultraviolet were also found effective. Among these are esculin and a number of naphtholsulfonic acids.

X-rays, ultraviolet radiations and α-rays cause the coagulation of sols of cerium hydroxide and albumin, and the inversion of cane sugar solutions, according to Fernau.[144]

Berlin blue hydrosols are decolorized and coagulated by visible and ultraviolet light. The time of flocculation by irradiation is proportional to the layer thickness and sol concentration; the optimum wave-length is 4200A.[145] Lal and Ganguly[146] found, however, that Prussian blue and gum mastic sols were not coagulated by the full radiation of the quartz mercury arc, although various sulfide sols (arsenic, cadmium, antimony, and ferrous), metallic sols (platinum, silver and gold), sulfur sols, hydroxides (cerium, thorium, ferric) were affected. The pH of the sols varied during exposure, some increasing and some decreasing. Coagulation was attributed to the destruction of stabilizing agents by the action of the light. These observations were extended by Miss Roy.[147] Sols of stannic, aluminum and

[140] Bhatnagar, S. S., Yajnik, N. A., and Zadoo, V. D., *Quart. J. Indian Chem. Soc.*, **4**, 209 (1927); *Chem. Abs.*, **21**, 3514 (1927).

[141] Krestinskaya, V., *Kolloid-Z.*, **66**, 58 (1934); *Chem. Abs.*, **28**, 1909 (1934).

[142] Joshi, C. B., Barve, P. M., and Desai, B. N., *Current Sci.*, **3**, 105 (1934); *Chem. Abs.*, **29**, 22 (1935).

[143] Boutaric, A., and Bouchard, J., *Compt. rend.*, **192**, 95, 357 (1931); **193**, 45 (1931); **194**, 1245 (1932); *Bull. Soc. Chim.*, **51**, 757 (1932); Pospelov, A., and Pospelova, K., *J. Phys. Chem. (U.S.S.R.)*, **5**, 52 (1934); *Chem. Abs.*, **28**, 4315 (1934).

[144] Fernau, A., *Kolloid-Z.*, **33**, 89 (1923); *Chem. Abs.*, **17**, 3837 (1923).

[145] Lederer, E. L., and Hartleb, O., *Kolloid-Z.*, **62**, 42 (1933); *Chem. Abs.*, **27**, 1800 (1933).

[146] Lal, P., and Ganguly, P. B., *J. Indian Chem. Soc.*, **6**, 547 (1929); *Chem. Abs.*, **24**, 540 (1930).

[147] Roy, S., *J. Indian Chem. Soc.*, **6**, 431 (1929); *Chem. Abs.*, **23**, 4865 (1929).

thorium hydroxides, of antimony, arsenious and mercuric sulfides, acquired increased conductivity after exposure, although uranium and cupric ferrocyanide sols did not. She found a short exposure to increase the stability of arsenious and antimony sulfides and uranium and cupric ferrocyanides, but on longer exposure all became less stable, and sols of antimony sulfide, mercuric sulfide and uranium ferrocyanide coagulated completely.

Heller[148] has considered the case in which the photochemical action is on the adsorbed electrolyte; coagulation is then probably due to the critical diminution of the double layer and the effect of light should be expected to be greater as the double layer is initially weaker. Sols of ferric oxide obtained by hydrolysis of ferric nitrate were dialyzed for three to twenty-five days and examined magneto-optically after varying periods in darkness followed by exposure to diffused light. The rate of growth of size of particles decreased with the time in darkness, but increased again on exposure to light, the increase being greatest in the sols longest dialyzed and so least stable.

Emulsions of benzene, benzine and carbon disulfide in water with sodium oleate as the emulsifier separated into two layers when irradiated with ultraviolet light.[149] The pH of the illuminated emulsion increased, indicating that its breaking was due to the partial destruction of the emulsifying agent.

Effects of Irradiation on Liesegang Ring Formation. Light of short wave-length is reported by Davies[150] to aid in the production of colored bands of colloidal gold in silicic acid gels containing gold chloride and various reducing agents. The work was extended by Cadenhead[151] to include the effects of x-rays. Both workers agree that the banding on reduction to colloidal gold is not a true Liesegang phenomenon. It has been observed[152] that the passage of a beam of light through soil or kaolin suspensions contained in a rectangular tank causes the suspensions to stratify, the layers running parallel to the surface. The distance between the successive strata appears to vary with the wave-length of the light, but the strata produced by white light are quite sharp. The stratification persists while the illumination is continued, and slowly disappears when it is cut off.

Blair[153] points out that in gels in either intense white light or complete darkness there is irregular Liesegang ring formation, which persists even after liquefaction and resetting. Ultraviolet rays from a quartz mercury lamp in a few hours render a gel incapable of Liesegang ring formation, but this effect does not persist after liquefaction.

Ultraviolet radiations cause a marked disturbance[154] in the rings formed round a drop of silver nitrate solution placed on a film of setting gelatin. X-rays and radium have no effect. The radiation restrains the primary rings and prevents the formation of secondary ones.[155] In the case of silver chromate-gelatin,[156] visible light causes the number of bands to increase and the distance between them

[148] Heller, W., *Compt. rend.*, **199**, 723 (1934).

[149] Sinha, P. C., and Ganguli, P. B., *Kolloid-Z.*, **54**, 147 (1931).

[150] Davies, E. C. H., *J. Am. Chem. Soc.*, **45**, 2261 (1923).

[151] Cadenhead, A. F. G., *Can. Chem. Met.*, **10**, 201 (1926); *Chem. Abs.*, **20**, 3390 (1926).

[152] Morrison, C. G. T., *Proc. Roy. Soc. London*, **108A**, 280 (1925).

[153] Blair, G. W. S., *Phil. Mag.*, **49**, 90 (1925).

[154] Cluzet, J., and Kofman, T., *Compt. rend. soc. biol.*, **104**, 1001 (1930); *Chem. Abs.*, **25**, 3245 (1931); see also Hatschek, E., *Kolloid-Z.*, **37**, 297 (1925); *Proc. Roy. Soc. London*, **96A**, 496 (1921) for similar observations on lead chromate bands.

[155] Kofman, T., *J. chim. phys.*, **29**, 586 (1932); *Compt. rend.*, **208**, 567 (1939).

[156] Isemura, T., *Bull. Chem. Soc. Japan*, **8**, 108 (1933); *Chem. Abs.*, **27**, 4152 (1933); Taboury, M.-F., and Bellot, M., *Compt. rend.*, **205**, 45 (1937). See also Teft, R., and Hill, J. W., *Trans. Kansas Acad. Sci.*, **33**, 57 (1931) for some effects of light on the formation of banded precipitates of mercuric iodide.

to shorten. Ultraviolet rays retard the formation of rings, which are finer and closer together than in the dark. Nikiforov and Lemeche [157] believe the "pressure" of Liesegang rings directly proportional to the light intensity. The number of rings per unit of distance increases under both ultraviolet and diffused daylight. Similar observations have been recorded by Miyamoto.[158] Chloride ions in definite concentrations seem to be necessary for light to have an effect on the production of the rings.[159]

It is held by Alekseevskii [160] that the adsorptive power of active charcoal and of silica gel is increased by irradiation with ultraviolet rays.

[157] Nikiforov, V.-K., *J. chim. phys.*, **32,** 585 (1935); Nikiforov, V.-K., and Lemèche, M.-R., *Ibid.*, **33,** 250 (1936).

[158] Miyamoto, S., *Kolloid-Z.*, **78,** 23 (1937).

[159] Köhn, M., and Mainzhausen, L., *Kolloid-Z.*, **79,** 316 (1937).

[160] Alekseevskii, E. V., *J. Russ. Phys.-Chem. Soc.*, **60,** 1173 (1928); *Chem. Abs.*, **23,** 2367 (1929).

Chapter 22

The Reactions of Organic Compounds. Aliphatic Series[1]

A very considerable body of empirical information has been accumulated regarding the photochemical behavior of a wide range of organic compounds, in large part due to the pioneering observations of Ciamician and Silber on the effects of prolonged exposures to sunlight and of Berthelot and Gaudechon on the effects of ultraviolet light. Unsaturated hydrocarbons rayed with ultraviolet undergo stereoisomeric transformations or polymerize. Alcohols, aldehydes and ketones decompose into carbon monoxide, hydrogen and hydrocarbons under some conditions. Acids may yield carbon dioxide and a hydrocarbon, with some carbon monoxide and hydrogen. Dibasic acids readily lose carbon dioxide, leaving monobasic acids. Keto acids react in ultraviolet when heated.

The theoretical interpretations of this behavior and its relation to the absorption spectra of the compounds studied has been most advanced in the case of the aldehydes and of the interconversions of geometrical isomers.

Saturated Hydrocarbons

The ultraviolet absorption spectra of the saturated hydrocarbons lies in the extreme ultraviolet. This accounts for the observed inertness of these compounds to the ordinarily available ultraviolet radiations.[2]

Methane is unaffected by the radiations between 2300 and 4000A.[3] With a Harteck xenon lamp giving 3×10^{16} quanta per second, the 1469A line is 13 per cent and the 1295A line 100 per cent absorbed by a 30-mm. layer of the gas at atmospheric pressure.[4]

The methane is decomposed in the primary process into methyl radicals and hydrogen atoms, the final products being hydrogen and acetylene, traces of ethylene, ethane and hydrocarbons with three to five carbon atoms.

Leighton and Steiner [5] also state that the radiation from a hydrogen discharge tube transmitted by a thin fluorite window decomposes methane with a quantum yield of the order of unity. They identified hydrogen and possibly ethylene in the approximate molecular ratio of four to one.

According to Tolloczko,[6] ethane irradiated in quartz with rays of wave-lengths between 2300 and 4000A gave a small amount of a light colorless condensate, composed of a mixture of hydrocarbons, mostly hexane; the gas contained hydro-

[1] For a general review, see Bonhoeffer, K. F., *Z. Elektrochem.*, **40,** 425 (1934).

[2] Glockler, G., *Proc. Nat. Acad. Sci.*, **11,** 74 (1925); Kemula, W., and Mrazek, S., [*Compt. rend.*, **195,** 1004 (1932)] found methane, ethane and butane not to absorb between 6000 and 1965A.

[3] Tolloczko, S., *Przemysl Chem.*, **11,** 245 (1927); *Chem. Abs.*, **22,** 4380 (1928).

[4] Groth, W., and Laudenklaus, H., *Naturwiss.*, **24,** 796 (1936); Groth, W., *Z. physik. Chem.*, **B38,** 366 (1937); see also Kemula, W., and Dyduszynski, A., *Roczniki Chem.*, **17,** 423 (1937); *Brit. Chem. Abs.* **A,** 39 (1938).

[5] Leighton, P. A., and Steiner, A. B., *J. Am. Chem. Soc.*, **58,** 1823 (1936).

[6] Tolloczko, S., *loc. cit.*

gen and methane. Klemenc and Patat [7] claim that pentane suffers decomposition and polymerization. The polymerization products take up oxygen, breaking the carbon chain and producing methane and carbon monoxide and dioxide.

Because of their transparency to ultraviolet rays, the liquid hydrocarbons are especially suitable solvents for use in measuring the absorption spectra of various organic solutes. Castille and Henri [8] have given detailed directions for the purification of hexane for this purpose. Samples of hexane prepared by their methods transmitted, in 40-mm. layers, to 1900A. Butane prepared by the Grignard method may contain an unidentified substance which shows fifteen absorption bands between 2206 and 1965A.[9] This impurity can be removed by long agitation with bromine water. In the Schumann regions, heptane and hexane have an absorption maximum at 1500A.[10] In the unsaturated compounds 1-heptylene, 2-pentylene, 1-pentylene, trimethylethylene, this is shifted to 1750A. These bands are without fine structure and are attributed to the dissociation of a carbon-carbon bond. Duncan and Howe [11] state that methane shows true continuous absorption in the region between 1450 and 850A, such continuous spectra being general for molecules with tetrahedral symmetry.

Mercury-sensitized reactions of ethane have recently been described by Kemula, Mrazek and Tolloczko.[12] Butane, hexane and octane are formed together with traces of methane. The proportion of butane in the product varies directly with the rate of flow and the pressure of the ethane, and inversely with the temperature of the receiver. Both the carbon-carbon and carbon-hydrogen linkings are affected. When butane is removed by a low-temperature trap, the reaction products, according to Steacie and Phillips, are exclusively methane, propane and butane. The quantum yield for ethane decomposed is 0.2.[13]

Taylor, Morikaw and Benedict [14] found that methane reacts with deuterium at 40° to 300°C. in the presence of mercury vapor excited by its resonance radiation. The degree to which the substitution occurs depends upon the time and temperature of irradiation. Farkas and Melville [15] proposed a chain mechanism for the reaction at temperatures over 300°C.:

$$D + XH \longrightarrow DX + H$$
$$H + D_2 \longrightarrow HD + D.$$

The oxidation of methane, methyl chloride and methylene chloride may be sensitized to light of the wave-length 4360A by chlorine.[16] The products from each of these compounds include carbon monoxide and hydrogen chloride, as well as small amounts of water, phosgene and several heavy volatile organic compounds. The quantum yield varies from 80 for methane to 800 for methylene chloride.

[7] Klemenc, A., and Patat, F., *Z. physik. Chem.*, **149A**, 449 (1930); see also Landau, M., *Compt. rend.*, **155**, 403 (1912); *J. Chem. Soc.*, **102**, II, 986 (1912).

[8] Castille, A., and Henri, V., *Bull. Soc. chim. biol.*, **6**, 299 (1924); the observations of Urbain, E., and Scal, C., [*Compt. rend.*, **168**, 887 (1919)] on the decomposition of saturated liquid hydrocarbons by ultraviolet rays may have been due to the presence of impurities.

[9] Kemula, W., and Mrazek, S., *loc. cit.*

[10] Carr, E. P., and Stücklen, H., *Helv. Phys. Acta*, **6**, 261 (1933).

[11] Duncan, A. B. F., and Howe, J. P., *J. Chem. Physics*, **2**, 851 (1934).

[12] Kemula, W., Mrazek, S., and Tolloczko, S., *Chem. Listy*, **26**, 466 (1932); *Chem. Abs.*, **27**, 3142 (1932).

[13] Steacie, E. W. R., and Phillips, N. W. F., *J. Chem. Phys.*, **6**, 179 (1938).

[14] Taylor, H. S., Morikaw, K., and Benedict, W. S., *J. Am. Chem. Soc.*, **57**, 383 (1935); *J. Chem. Phys.*, **5**, 212 (1937).

[15] Farkas, A., and Melville, H. W., *Proc. Roy. Soc.*, **157A**, 625 (1936).

[16] Brenschede, W., and Schumacher, H. J., *Z. physik. Chem.*, **177A**, 245 (1936).

These are all chain reactions, involving the formation of intermediate, short-lived peroxides. Methane and methyl chloride also suffer chlorination to methylene chloride, some molecules of which on colliding with chlorine atoms form the $CHCl_2$ radical. This, reacting with oxygen, goes through various intermediate compounds to carbon monoxide and hydrogen chloride. The reactions of methane and methyl chloride, but not that of methylene chloride, are inhibited by an excess of oxygen.[17]

Cyclopropane undergoes a mercury-sensitized photochemical polymerization to a colorless oil of high boiling point under the influence of the resonance line of mercury.[18] The I. G. Farbenindustrie A.-G [19] claims the conversion of cyclohexanone into caproic acid by irradiation.

Alkyl Halides

Absorption Data. The absorption of methane is gradually shifted to longer wave-lengths as the number of halogen atoms introduced is increased.[20] However, most alkyl halides absorb but slightly. The bromides absorb more and at longer wave-lengths than the chlorides, methyl bromide absorbing nearly as well as carbon tetrachloride. The foot of the absorption curve of carbon tetrabromide approaches the visible spectrum. The iodine compounds absorb still more readily, iodoform absorbing in the visible portion of the spectrum.

Herzberg and Scheibe [21] found methyl iodide, bromide and chloride to show continuous absorption bands, with maxima at 2500, 2000, and 1750A, attributed to dissociation of the molecule into the methyl group and a halogen atom, one of the products being in an excited state. Iredale and Mills [22] found the energies of the carbon-to-iodine and carbon-to-bromine linkings, as calculated from the long wave-length limits of the continuous bands, to be in good agreement with the values calculated from the heats of combustion.[23]

Hukumoto,[24] who made similar calculations, reported data on the continuous absorption spectra of about forty alkyl halides. The iodides exhibited two or three absorption regions, the one with longest wave-lengths corresponding to a decomposition into a normal alkyl radical and an iodine atom in the metastable $2^2P_{1/2}$ state. The excess energy in the second and third continuous absorption regions was thought to be associated with excitation of the alkyl radicals.

Parti and Samuel [25] interpret the absorption spectrum of methyl iodide as involving a simultaneous loss of a hydrogen and an iodine atom. They pointed out that the beginnings of the first selective absorption of twelve alkyl halides agree with the estimated energy differences $D(CX_4) - D(CX_2)$. This viewpoint, based on an analogy with the behavior of the tin halides, appears to involve a consid-

[17] Schumacher, H. J., *Z. Elektrochem.*, **42**, 522 (1936).

[18] Harris, L., Ashdown, A. A., and Armstrong, R. T., *J. Am. Chem. Soc.*, **58**, 852 (1936).

[19] I. G. Farbenindustrie A.-G., British P. 314,267, 1928.

[20] Lowry, T. M., and Sass, R. B., *J. Chem. Soc.*, 622, 1926.

[21] Herzberg, G., and Scheibe, G., *Trans. Faraday Soc.*, **25**, 716 (1929); *Z. physik. Chem.*, **7B**, 390 (1930).

[22] Iredale, T., and Mills, A. G., *Proc. Roy. Soc.*, **133A**, 430 (1931). See also *Z. physik. Chem.*, **20B**, 340 (1933).

[23] For details of the calculation of the heats of dissociation of the carbon-halogen bond by this method, see also Sen-Gupta, P. K., *Bull. acad. Sci. United Provinces Agra Oudh, India*, **2**, 115 (1933); *Chem. Abs.*, **27**, 3668 (1933).

[24] Hukumoto, Y., *Phys. Rev.*, **42**, 313 (1932); *Science Repts. Tohoku Imp. Univ. First Ser.*, **22**, 13 (1933); **21**, 906 (1932). Data on methyl bromide are given by Fink, P., and Goodeve, C. F., *Proc. Roy. Soc.*, **A163**, 592 (1937).

[25] Parti, Y., and Samuel, R., *Current Sci.*, **5**, 386 (1937); *Chem. Abs.*, **31**, 3385 (1937); Bergmann, E., and Samuel, R., *Nature*, **141**, 832 (1938).

erable revision of the current theories of the photochemical processes in which the alkyl halides participate.

As determined by Saha,[26] who obtained the limit of continuous absorption from spectrograms by the method of Herzberg and Scheibe, the wave-length limits and their values in kcal. for the C—Cl bond are in carbon tetrachloride, 2800A, 102, in chloroform, 2660A, 107.5, and in methylene chloride, 2500A, 114.4 kcal. These results are considered as in good agreement with those calculated thermochemically, if allowance be made for uncertainty as to the energy state of the carbon atom.[27]

The alkyl halides also exhibit discontinuous absorption beginning at 2010, 1785 and 1600A for methyl iodide, bromide and chloride, respectively, according to Herzberg and Scheibe.[28] The discontinuous bands are considered to indicate transitions into several excited electronic states.[29]

Reactions. Although early observers made frequent reference to the decomposition of alkyl halides in light,[30] Stobbe and Schmitt [31] showed that the effects noted in daylight were due to an oxidation. In the absence of oxygen the halides are relatively light-stable. They did, however, show that a photochemical liberation of bromine from ethyl bromide occurs in the short wave-length ultraviolet to a slight extent. Similar reactions occur also with the iodides, isopropyl iodide being less stable than either *n*-propyl, ethyl or methyl iodides.

The products formed when ethyl iodide is photochemically decomposed in the absence of oxygen include, according to Emschwiller and Job,[32] besides iodine, a gas composed principally of ethylene and ethane, with smaller amounts of butane and hydrogen. The formation of the butane could be explained as due to a combination of two ethyl radicals liberated in the primary process. The ethylene and ethane were accounted for by assuming that the primary process for the most part consists in a simultaneous loss of both hydrogen and iodine atoms from the ethyl iodide as hydrogen iodide, leaving ethylene. (The ethane might then arise by combination of ethylene with hydrogen produced by the photodecomposition of the hydrogen iodide.[33]) In similar fashion, propyl iodide yielded propylene and propane, normal, secondary and isobutyl iodides gave butylene and butane, and methyl iodide gave methane. Tertiary butyl iodide gave propylene and propane, ethylene and ethane. In these experiments the alkyl halides were irradiated as liquids. Emschwiller believed both the hydrogen and the iodine atoms to be liberated from the same carbon atom, the residue rearranging to give the olefine. He also believed studies of the photochemical oxidation of the alkyl halides to corroborate this conception, methyl iodide, ethyl iodide and isopropyl iodide giving formaldehyde, acetaldehyde and acetone, respectively.[34] It may be noted that Emschwiller's conception of the primary process is in agreement with that of Parti

[26] Saha, N. K., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 233 (1933); *Chem. Abs.*, **27**, 4733 (1933). For further data on other halides, see Rehman, R. A., Samuel, R., and Sharf-ud-Din, *Indian J. Physics*, **8**, 537 (1934); Price, W. C., *Phys. Rev.*, **47**, 419 (1935); *J. Chem. Physics*, **3**, 365 (1935); **4**, 547 (1936).

[27] For the absorption spectra of more complex halides, see Fukumoto, Y., *Science Repts., Tohoku Imp. Univ. First Series*, **23**, 62 (1934).

[28] Also Scheibe, G., Povenz, F., and Lindström, C. F., *Z. physik. Chem.*, **20B**, 283 (1933).

[29] See also Henrici, A., *Z. Physik*, **77**, 35 (1932) and for the theoretical interpretation of the methyl iodide bands, Mulliken, R. S., *Phys. Rev.*, **47**, 413 (1935), and Porret, D., and Goodeve, C. F., *Trans. Faraday Soc.*, **33**, 690 (1937); *Proc. Roy. Soc.*, **A165**, 31 (1938).

[30] Schoorl, N., and Van den Berg, L. M., *Pharm. Weekblad.*, **43**, 218 (1906); Benrath, A., *Annalen*, **382**, 222 (1911).

[31] Stobbe, H., and Schmitt, P., *Z. wiss. Phot.*, **20**, 57 (1920).

[32] Emschwiller, G., and Job, A., *Compt. rend.*, **179**, 52, 168 (1924).

[33] Emschwiller, G., and Job, A., *Compt. rend.*, **192**, 799 (1931); **193**, 1003 (1931).

[34] Emschwiller, G., and Job, A., *Ann. Chim.*, **17**, 413 (1932).

and Samuel, although the latter workers do not postulate a rearrangement of the radical with divalent carbon to an olefin.

On the other hand, Bates and Spence [35] believe the primary process, at least in the case of gaseous methyl iodide, to consist solely in a simple dissociation into a free methyl radical and an iodine atom.[36] They also support this by a study of the reaction occurring in the presence of oxygen. In this case the methyl radical may react with oxygen to produce formaldehyde and an hydroxyl radical. The latter, on reaction with a fresh methyl iodide molecule yields methanol and an iodine atom. Methanol (two molecules) and formaldehyde may then react to produce methylal, $(CH_3O)_2CH_2$, and water. Furthermore, Spence and Wild [37] found the irradiation of pure methyl iodide in the absence of oxygen to yield no hydrogen iodide. Small amounts of methane, ethane and iodine were formed.[38] The presence of free methyl radicals in the photochemical decomposition of methyl iodide vapors has been recently demonstrated by the ortho-para hydrogen conversion test for the presence of paramagnetic substances.[39]

In his earlier work, Emschwiller [40] believed that a critical threshold wave-length for the ethyl iodide and methyl iodide decompositions had been observed at 4100A. In later observations, however, he gave up the concept of the existence of a threshold value since he had found the absorption curve of ethyl iodide to vary with the temperature, being shifted toward the visible by about 12A per 10°C.[41]

The quantum yields obtainable under various conditions have been a matter of controversy. Bates and Spence [42] found that methyl iodide vapors, when irradiated in the continuum, gave the very low quantum yield of 0.02. It was slightly greater (0.05) in hexane solution. Spence and Wild [43] put the yield of methane from methyl iodide vapor at 0.032, that of free iodine being half as great. Calculated as methyl iodide destroyed, the quantum yield is at least 0.06. Higher iodides are probably formed. The reaction is not affected by the addition of hydrogen or nitrous oxide.

Very similar results have been recorded for ethyl iodide, although Emschwiller gave yields at high temperatures for ethyl iodide seventeen or more times as great as for methyl iodide. Norton [44] found for liquid ethyl iodide the values 0.315 at 3130A, 0.38 at 2654A and 0.41 at 2537A. The higher yields of about unity reported by Iredale were believed to have been due to the presence of some oxygen.[45]

[35] Bates, J. R., and Spence, R., *J. Am. Chem. Soc.*, **53**, 381, 1689 (1931); *Trans. Faraday Soc.*, **27**, 468 (1931).

[36] A general discussion of free radicals in organic photoprocesses is due to H. S. Taylor, *J. Phys. Chem.*, **42**, 763 (1938).

[37] Spence, R., and Wild, W., *Proc. Leeds Phil. Lit. Soc., Sci. Section*, **3**, 141 (1936); *Chem. Abs.*, **30**, 2849 (1936). In the presence of hydrogen iodide, methyl iodide yields iodine with a quantum yield of two, according to Iredale, T., and Stephan, D., *Trans. Faraday Soc.*, **33**, 800 (1937).

[38] Jones, L. T., and Bates, J. R., [*J. Am. Chem. Soc.*, **56**, 2285 (1934)] found the kinetics of the rapid photooxidation of ethyl iodide to differ from that of methyl iodide. Acetaldehyde and ethanol were produced. A mechanism involving the intermediary formation of ethyl peroxide was proposed, but the observation of small deviations in the rates from those expected suggested the reaction to be one of great complexity.

[39] West, W., *J. Am. Chem. Soc.*, **57**, 1931 (1935). It also is found in the acetone decomposition, but negative tests were obtained in the irradiation of benzene and of propionaldehyde vapors.

[40] Job, A., and Emschwiller, G., *Compt. rend.*, **179**, 52,168 (1924).

[41] Job, A., and Emschwiller, G., *Compt. rend.*, **190**, 741,866 (1930); *Ann. Chim.*, **17**, 413 (1932).

[42] Bates, J. R., and Spence, R., *J. Am. Chem. Soc.*, **53**, 1689 (1931).

[43] Spence, R., and Wild, W., *Proc. Leeds Phil. Lit. Soc., Sci. Section* **3**, 141 (1936); *Chem. Abs.*, **30**, 2849 (1936).

[44] Norton, B. M., *J. Am. Chem. Soc.*, **56**, 2294 (1934).

[45] Iredale, T., *J. Phys. Chem.* **33**, 290 (1929). It must be noted, however, that Gibson, K. E., and Iredale, T. [*Trans. Faraday Soc.*, **32**, 571 (1936)] have found a value of unity for benzene solutions of methyl iodine in the absence of oxygen in recent redeterminations. The same value was given by γ-butyl iodide. In alcohol, methyl iodide gave values greater than one. Furthermore, iodoform in benzene gave a value of one in the absence of oxygen and higher in its presence. In alcohol, the yields seemed higher.

West and Paul[46] found the quantum yields in hexane to be a constitutive property of the alkyl group,[47] varying from a few hundredths in the case of methyl iodide to slightly over one for isopropyl iodide for the wave-length 2610A.[47a] The yield increases somewhat with decreasing wave-lengths between 3130 and 2610A, the ratios differing, however, for each of five iodides studied. They concluded a direct recombination of the iodine atom and the free radical to be the cause of the low yield for methyl iodide. (The non-dependence of the yield on the concentration made it seem that the reaction $CH_3 + CH_3I \rightarrow C_2H_6 + I$ is uncommon. Similarly, the reaction between an iodine molecule and a free methyl radical was thought to be infrequent because of the zero order of the reaction in its early stages.) Accordingly, it was suggested that the values of the quantum yields shown by the various halides might give directly the relative probabilities of recombination of the various alkyl radicals with atomic iodine. If this be admitted, the order of reactivity of the alkyl radicals would be methyl > allyl > vinyl > ethyl > propyl > isopropyl.

West and Ginsburg[48] found that, although in the pure liquid state or in hexane solution, ethyl iodide decomposes with a quantum yield of 0.6, in the vapor state the quantum yields at 2600A in the continuum are very low.

They also made observations of the quantum yields at the beginning of the short wave-length region of banded absorption at 2026A. In the vapor at 45 or 90 mm. pressure at 30°C., the yield was 0.1. At 0.1 mm. it was definitely lower, and was also lower than that of the reaction produced by this wave-length in condensed phases, the yield in the liquid being about 0.24. In the short wave-length region, interaction between excited molecules and normal molecules seemed the predominant mechanism.

Especial attention was paid, by West and Schlessinger,[49] to the products other than iodine. They found that at 2537A methyl iodide yields mostly methane and small quantities of ethylene and ethane, and that more than a third of the iodide decomposed appears as methylene iodide. Addition of silver foil increases the rate of reaction about fortyfold, yields all the iodine as silver iodide, and causes the gaseous products to consist mostly of ethane with some ethylene but much less methane than in the absence of silver. Ethyl iodide at 2537A gives ethane and ethylene in comparable proportions. At 2026A, small amounts of methane and hydrogen are also formed. Silver increases the reaction rate but does not affect the nature of the products. Inert gas up to 40 atmospheres increases the iodine yield linearly with the density of inert gas to values approaching one-third the yield in inert liquid solvents. The primary process forms iodine atoms and alkyl radicals. Recombination of these, which may occur as a bimolecular process, is the most rapid secondary process and accounts for the low quantum yields. Most of the net change is due to the reaction:

$$R' + R''H_2I \longrightarrow R'H + R''HI$$

This predominates over the association of R to R_2 and I to I_2. The quantum yield of *n*-propyl iodide vapor at 2026A is lower than that of ethyl iodide; the yields for isopropyl iodide at 2610 and 2026A are 0.17 and 0.43, respectively.

[46] West, W., and Paul, B., *Trans. Faraday Soc.*, **28**, 688 (1932).

[47] Note also Burke, K. A., and Donnan, F. G., *J. Chem. Soc.*, **85**, 574 (1904).

[47a] Norton also notes that the quantum yield increases in various alkyl halides as the chain is lengthened, as the central carbon atom is altered from primary to tertiary and as halogen atoms are progressively introduced.

[48] West, W., and Ginsburg, E., *J. Am. Chem. Soc.*, **56**, 2626 (1934).

[49] West, W., and Schlessinger, L., *J. Am. Chem. Soc.*, **60**, 961 (1938).

According to Maynard,[50] the direct union of metallic mercury and methyl iodide is not hastened by ultraviolet rays but is accelerated by a specially arranged arc light. The reaction is preceded by the formation of a small amount of mercurous iodide. If the latter is irradiated together with methyl iodide, methyl mercuric iodide is formed rapidly. Although the action of metallic mercury is not encountered in the case of the other alkyl halides, the use of mercurous iodide makes possible the extension of the reaction to higher iodides and even to benzyl iodide.

Ramart-Lucas and Salmon-Legagneur[51] find ultraviolet light capable of converting isobutyl bromide into *tert*-butyl bromide, and propyl bromide into isopropyl bromide without any trace of dissociation occurring.

Irradiation of the vapor of methylene iodide and oxygen by the quartz mercury arc yields such products as carbon monoxide, hydrogen, iodine, formaldehyde, formic acid and ethylene glycol. The quantum yield with respect to iodine is 1.45 for light of wave-length 3100A. Gregory and Style[52] suggest CH_2, CH_2O_2 and $(CH_2O)_2$ as intermediates, the two latter substances changing into formic acid and formaldehyde, respectively. Emschwiller[53] finds iodine pentoxide to be formed particularly while some of the methylene iodide remains unattacked; it may result through the intermediary formation of peroxides of formaldehyde, formic acid, or possibly of methylene iodide.

According to Kaufmann,[54] *trans*- and *cis*-α,β-diiodoethylene and α,α'-diiodoethylene are decomposed with liberation of iodine when their ether solutions are exposed to ultraviolet, the velocity of the reaction in the first being approximately twice as great as that in the other two cases.

Solutions of ethylene iodide in carbon tetrachloride begin to absorb at 3600A, the absorption increasing at shorter wave-lengths. DeRight and Wiig[55] found the rate of the direct decomposition due to the absorption of the wave-lengths 3130 and 3030A approximately proportional to the absorbed energy. It increased slightly with increasing concentrations of the ethylene iodide, reached a definite maximum after the attainment of a certain amount of decomposition, and was reduced by the addition of iodine. The primary decomposition was assumed to yield atomic iodine and C_2H_4I. The quantum yield was 0.76 and the temperature coefficient 1.05. Emschwiller[56] observed[57] that vinyl iodide, irradiated 124 hours by a mercury vapor lamp, gave acetylene, ethylene and iodine and, in the presence of oxygen, also formed droplets of liquid containing formic acid, formaldehyde and $CH_2OH{\cdot}CHO$. He suggested a different mechanism for the decomposition of asymmetrical ethylene diiodide:

$$2CH_2 = CI_2 \longrightarrow C_2H_2 + C_2I_2 + 2HI.$$

$$CH_2 = CI_2 + HI \longrightarrow CH_3CI_3.$$

He also found that although CHI = CHI is not oxidized in ultraviolet light, its asymmetrical isomer is completely oxidized with the formation of formic acid, a

[50] Maynard, J. L., *Science*, **56**, 492 (1922).

[51] Ramart-Lucas, Mme., and Salmon-Legagneur, F., *Compt. rend.*, **186**, 39 (1928); see also Emschwiller, G., *Ann. Chim.*, **17**, 413 (1932).

[52] Gregory, R. A., and Style, D. W. G., *Trans. Faraday Soc.*, **32**, 724 (1936).

[53] Emschwiller, G., *Compt. rend.*, **206**, 746 (1938).

[54] Kaufmann, H. P., *Ber.*, **55**, 249 (1922).

[55] DeRight, R. E., and Wiig, E. O., *J. Am. Chem. Soc.*, **57**, 2411 (1935).

[56] Emschwiller, G., *Compt. rend.*, **198**, 1151 (1934).

[57] Emschwiller, G., *Compt. rend.*, **198**, 464 (1934).

trace of formaldehyde, iodine and a gas composed of 57 per cent carbon monoxide, 23 per cent carbon dioxide and 20 per cent acetylene.

An iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride is discussed by Dickinson and Nies.[58] Emschwiller[59] writes for the decomposition of diiodoethane,

$$CH_2CHI_2 + h\nu \longrightarrow CH_2 = CHI + HI$$
$$CH_2CHI_2 + HI \longrightarrow CH_3CH_2I + I_2$$

Both products then decompose with the separation of iodine, so that the complete reaction may be written:

$$4CH_2CHI_2 \longrightarrow C_2H_2 + 2C_2H_4 + C_2H_6 + 4I_2.$$

The ethylene then mostly forms ethylene iodide. In the presence of oxygen, both diiodoethane and unsymmetrical diiodoethylene are completely oxidized. The analogy of structure between diiodomethane and diiodoethane implied by a similarity of decomposition is confirmed by the similarity of their absorption spectra and by the rapid photochemical oxidation of diiodomethane.

Iodoform, although said to be very light-stable in the absence of oxygen, may in benzene solution yield some iodine and hydriodic acid in daylight.[60] Chloroform is also stable, although it exhibits a continuous absorption beginning at 2530A (1 cm. of liquid) or at 2300A (50 cm. of vapor at 1 mm.). Hill[61] was unable to detect any decomposition in a static system. In streaming vapor, chlorine could not be detected, but hydrogen chloride was formed. There was evidence of a short-chain reaction, yielding four molecules per quantum absorbed. The yield was not affected by the presence of hydrogen. It seemed to be increased by nitrogen and was very greatly increased by oxygen, but in the latter case the mechanism is doubtless changed. Binz and Hughes[62] have suggested that sodium triiodomethanesulfonate, proposed for x-ray work in urological diagnosis, may owe its observed toxicity to the ease with which it splits off iodine in light.

Carbon tetrachloride has been suggested as an actinometric compound for standardizing the ultraviolet output of mercury arcs,[63] at wave-lengths less than about 2650-2750A, but Hymas[64] could not obtain satisfactory results with it. According to Benrath and Hertel,[65] decomposition may be represented as

$$2CCl_4 \longrightarrow C_2Cl_6 + Cl_2$$

the reaction occurring in the liquid exposed in an open vessel. In a recent investigation, Lyons and Dickinson[66] found that in the absence of oxygen, pure carbon tetrachloride underwent practically no decomposition when exposed to the 2537A line, the quantum yields being less than 0.01. In the presence of oxygen, however, phosgene and chlorine were produced in equimolar proportions, the quantum yield being close to unity.

[58] Dickinson, R. G., and Nies, N. P., *J. Am. Chem. Soc.*, **57**, 2382 (1935).
[59] Emschwiller, G., *Compt. rend.*, **199**, 854 (1934).
[60] Dubrisay, R., and Emschwiller, G., *Compt. rend.*, **195**, 660 (1932).
[61] Hill, D. G., *J. Am. Chem. Soc.*, **54**, 32 (1932); see also Massol, G., and Faucon, A., *Compt. rend.*, **159**, 314 (1914); *Bull. soc. chim.*, **19**, 350 (1916).
[62] Binz, A., and Hughes, B., *Ber.*, **68B**, 1513 (1935).
[63] MacKenzie, T. C., and King, A. A., "Practical Ultraviolet Light Therapy," New York, Wood 1926.
[64] Hymas, F. C., *Quart. J. Pharm.* **2**, 281 (1929).
[65] Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924).
[66] Lyons, E. H., Jr., and Dickinson, R. G., *J. Am. Chem. Soc.*, **57**, 443 (1935).

Trichloroethylene may be oxidized in the presence of chlorine as sensitizer by the 4360A line.[67] The yield of dichloroacetyl chloride is not greater than 95 per cent. The rate varies with the light intensity, but is independent of the trichloroethylene and oxygen concentrations. The quantum yield is about 40 at 95°. A peroxide, $C_2HCl_4O_2$, may be a part of the chain.

In the case of tetrachloroethane,[68] the reaction probably consists in a primary decomposition into HCl and $CHCl_2CCl$, the latter then reacting with oxygen to form dichloracetyl chloride, which is hydrolyzed by moisture to dichloracetic acid. Oxygen also removes a hydrogen atom from the original halide, and the $CHCl_2CCl_2$ residues combine to form octachlorobutane. In dry air, a fuming liquid, dichloracetyl chloride, could be obtained. The reactions were shown not to be due to ozone produced by the action of the light upon the oxygen. In the presence of nitrogen rather than air, no reaction whatever occurred, not even the evolution of hydrogen chloride.[69] The same was true of the compounds $CHCl_2CCl_3$ and $CCl_2{=}CHCl$. The reaction was therefore assumed to be brought about by activated oxygen. Further evidence for this mechanism is found in the fact that the compound $(CH_2Cl)_2$ can react, although it does not absorb in the wave-length range employed. In the presence of dry oxygen in short wave-length light, it gives monochloracetic acid.[70]

Attention has been called to a bromine-sensitized photochemical decomposition of dibromotetrachloroethane by Carrico and Dickinson.[71] It proceeds as a chain reaction with quantum yields which, at low intensities, are independent of the intensity, but which fall off at higher intensities.

There is a bromine-sensitized oxidation of carbon tetrabromide in carbon tetrachloride, produced by the 4360A line, which may be expressed by

$$2CBr_4 + O_2 \rightarrow 2COBr_2 + 2Br_2.$$[72]

Not more than 50 kcal. is required to remove the first bromine atom.

Alcohols

Bielecki and Henri[73] found the absorption of ethyl alcohol to begin at about 2500A.

Several new methods for the purification of alcohol for use as a solvent in absorption spectroscopy were tested by Leighton, Crary and Schipp.[74] They found the threshold absorption furthest in the ultraviolet for samples which had been allowed to stand for one week over active aluminum amalgam, filtered and distilled. Their results were in general confirmed by Harris,[75] who preferred, however, to modify the method of preparation introduced by Castille and Henri[76] by carrying out the final distillation with the aid of zinc wool rather than zinc powder.

Herzberg and Scheibe[77] found that both methanol and ethanol vapors show

[67] Müller, K. L., and Schumacher, H. J., *Z. physik. Chem.*, **37B**, 365 (1937).
[68] Müller, E., and Luber, A., *Ber.*, **65B**, 985 (1932).
[69] Müller, E., and Ehrmann, K., *Ber.*, **69B**, 2207 (1936).
[70] Aromatic compounds with halogen in the side chain behave similarly, benzyl chloride slowly changing into benzoic acid and $C_6H_5CHCl_2$ yielding benzoyl chloride.
[71] Carrico, J. L., and Dickinson, R. G., *J. Am. Chem. Soc.*, **57**, 1343 (1935).
[72] Koblitz, W., Meissner, H., and Schumacher, H. J., *Ber.*, **70B**, 1080 (1937).
[73] Bielecki, J., and Henri, V., *Ber.*, **45**, 2819 (1912); *Compt. rend.*, **155**, 456 (1912).
[74] Leighton, P. A., Crary, R. W., and Schipp, L. T., *J. Am. Chem. Soc.*, **53**, 3017 (1931).
[75] Harris, L., *J. Am. Chem. Soc.*, **55**, 1940 (1933).
[76] Castille, A., and Henri, V., *Bull. soc. chim. biol.*, **6**, 299 (1924); *Chem. Abs.*, **18**, 3165 (1924).
[77] Herzberg, G., and Scheibe, G., *Z. physik. Chem.*, **7B**, 390 (1930).

continuous absorption beginning at about 2000A and extending to 1500A. They believed a decomposition into alkyl and hydroxyl radicals to be probable. Terenin and Neuĭmin [78] find that methanol when decomposed in the Schumann region emits bands indicative of the presence of hydroxyl radicals in excited states. From studies of the continuous absorption of a number of alcohols in the vapor state, Fukumoto [79] reports the energy of dissociation of the carbon to hydroxyl bond to vary from 133.6 to 152.2 kcal. per mole for the series from methanol to n-$C_{12}H_{25}OH$. For the isomers of butyl alcohol, no regularity was to be found in the energy of this bond, although it was at a maximum, 141.9 kcal., in the normal alcohol.

The alcohols are stable to ultraviolet rays,[80] unless the wave-lengths be shorter than about 2000A. Methanol and ethanol are decomposed by such wave-lengths.[81] Methanol gives some formaldehyde, but most is decomposed into hydrogen and carbon monoxide. Indeed, the products of the alcohol [82] decomposition are said to be about 80 per cent hydrogen and 20 per cent carbon monoxide. (Ethanol gives hydrogen and acetaldehyde.) There is as yet no evidence for the formation of atomic hydrogen. The quantum yield is between one and two.[83] From the failure of the para-ortho hydrogen test for free radicals, Patat did not believe the primary process could be the dissociation of the carbon-hydroxyl bond suggested by spectroscopic observations.

Elhart and Orth [84] state that goldfish are anesthetized more rapidly in methanol or ethanol solutions when these are irradiated because of the formation of aldehyde and acid.

Cantieni [85] finds that in the presence of oxygen, methanol forms peroxide in the absence of water, the presence of which retards its formation. The peroxide CH_3OOH is assumed to oxidize methanol in the presence of ultraviolet light with the production of traces of formaldehyde. Peroxide formation occurs most rapidly with isoalcohols, rapidly with methanol and more slowly in the remaining normal alcohols. In ultraviolet light of longer wave-lengths the rate of formation of peroxides increases with an increase in the number of carbon atoms in the alcohol. Cantieni also finds glycol to form a peroxide $HO{\cdot}CH_2CH_2O_2H$. This, reacting with excited glycol molecules, gives carbon dioxide, water and glycol.[86]

According to Henri and Ranc,[87] glycerol, as such or better in aqueous solutions, suffered some decomposition, especially in the presence of air. A small quantity of a substance giving a positive phloroglucinol reaction for glyceric aldehyde was formed. In alkaline solution, β-acrose was apparently identified by means of the phenylosazone. Its amount could possibly be increased by the

[78] Terenin, A., and Neuĭmin, H., *Nature,* **134,** 255 (1934); *J. Chem. Physics,* **3,** 436 (1935).

[79] Fukumoto, Y., *Nature,* **134,** 538 (1934).

[80] Berthelot, D., and Gaudechon, H., *Compt. rend.,* **156,** 68 (1913); Volmar, *Compt. rend.,* **182,** 1607 (1926).

[81] Patat, F., *Anz. Akad. Wiss. Wien. Math-naturw. Kl.,* 93 (1933); *Chem. Abs.,* **28,** 6371 (1934); Patat, F., and Hoch, H., *Z. Elektrochem.,* **41,** 494 (1935).

[82] Fricke, H., and Hart, E. J., *J. Chem. Physics,* **4,** 418 (1936) believe methanol to give directly hydrogen and formaldehyde.

[83] 0.8 for ethanol in solution, according to Farkas, L., and Hirschberg, Y., *J. Am. Chem. Soc.,* **59,** 2450 (1937). Isopropyl alcohol yields acetone and hydrogen. One of the hydrogen atoms comes from the OH and the other from C—H.

[84] Elhart, W., and Orth, O. S., *Anesthesia and Analgesia,* **14,** 15 (1935); *Chem. Abs.,* **29,** 3401 (1935).

[85] Cantieni, R., *Ber.,* **69B,** 1101, 1386 (1936). *Cf.* Milas, N., U. S. P. 2,115,206-7, April 26, 1938; *Chem. Abs.,* **32,** 4606 (1938).

[86] Cantieni, R., *Z. wiss. Phot.,* **36,** 116 (1937).

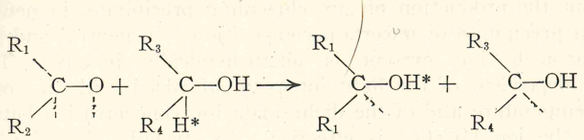
[87] Henri, V., and Ranc, A., *Compt. rend.,* **154,** 1261 (1912); Bierry, H., Henri, V., and Ranc, A., *Ibid.,* **152,** 535 (1911).

addition of salts of iron, cobalt or uranium before the irradiation. Formaldehyde and acids were also formed.[88] Cantieni [89] finds glycerol irradiated in solutions of various concentrations, to give carbon dioxide and water, a peroxide $OH{\cdot}CH_2CH(OH)CH_2OOH$ being postulated as an intermediate product. The evidence for the formation of the intermediate in this and other alcohol oxidations consisted in a titanium sulfate titration.

The oxidation of ethyl alcohol can be photosensitized by the addition of hydrogen peroxide. The oxidation is a chain reaction of short chain length, compatible with that of the chains postulated in the Haber-Willstätter mechanism of the chain reactions set up in the enzymatic oxidation of alcohol.[90]

The hydrogen peroxide-sensitized oxidation of mannitol known to Henri and Ranc, (l.c.) has recently been studied by Salley.[91] At a constant initial hydrogen peroxide concentration, increase in the mannitol concentration causes an increase in the rate of absorption of oxygen and a simultaneous decrease in the rate of decomposition of the hydrogen peroxide. At a sufficiently high mannitol concentration, however, the rates of both reactions become independent of the mannitol concentration. Since a maximum of two molecules of oxygen can be absorbed for each molecule of hydrogen peroxide which disappears, the photosensitized oxidation of the mannitol does not appear to be a chain process. In the presence of ethylamine, an inhibitor of the photolysis of hydrogen peroxide, the rate of the decomposition of the peroxide in the mannitol mixture is increased. At the same time, the rate of absorption of oxygen apparently decreases, probably owing to the destruction of the hydrogen peroxide with some evolution of oxygen.

Ketones and alcohols undergo mutual oxidation in light, according to Weizmann, Bergmann and Hirschberg,[92] who cite the earlier observations. Acetophenone and butanol give the pinacol of acetophenone, butanol being dehydrogenated to butyraldehyde. Acetophenone reacts in an analogous fashion with cyclohexanol, phenylmethylcarbinol, ethanol and isopropanol. The system cyclohexanone-cyclohexanol gives but a poor yield of cyclohexanone pinacol. The system acetone-butanol gave two isomeric forms of *sym*-dipropylglycol, and, in the first fractions of the reaction product, butyraldehyde and isopropanol. It is assumed that the first step in these processes is the activation of the carbonyl compound leading to a diradical form which reacts with the carbinol, splitting the C—H bond and giving two radicals. These subsequently stabilize by symmetrical or unsymmetrical dimerization or by a second oxidation-reduction process.



A photocatalytic influence of ketones on the velocity of oxidation of ethyl and other alcohols was described by Cohen.[93] The velocity was found to be inde-

[88] Henri, V., and Ranc, A., *Compt. rend.,* **151,** 316 (1910); *Biochem. Z.,* **64,** 257 (1914).

[89] Cantieni, R., *Ber.,* **69B,** 1796 (1936).

[90] Taylor, H. S., and Gould, A. J., *J. Am. Chem. Soc.,* **55,** 859 (1933); *J. Phys. Chem.,* **37,** 367 (1933).

[91] Salley, D. J., *J. Phys. Chem.,* **38,** 465 (1934).

[92] Weizmann, C., Bergmann, E., and Hirschberg, Y., *J. Am. Chem. Soc.,* **60,** 1530 (1938).

[93] Cohen, W. D., *Proc. Acad. Sci. Amsterdam,* **26,** 443 (1923); *Chem. Abs.,* **14,** 2785 (1920); **15,** 3617 (1921); **18,** 50 (1924); Boeseken, J., *Rec. trav. Chim.,* **40,** 433 (1921); **39,** 243 (1920). See also Chapter 25.

pendent of the concentration of the ketone within wide limits and proportional to the alcohol concentration.[94] The ketone itself either remains unchanged or forms a pinacone. Either benzophenone, aliphatic α-diketones or α, β-diketones with an aromatic nucleus could be employed. No absorption peak in the ketone spectrum appeared to coincide with the wave-length range which proved active (4000-4100A).

Boeseken and Langedijk employed the reaction to effect a partial asymmetric synthesis. The *l*-menthyl ester of *o*-$PhCOC_6H_4COOH$ was used to catalyze the oxidation of racemic methylethylcarbinol and caused after a hundred hours a levorotation of between 0.03 and 0.04° in a 20-cm. tube.

Berthoud[95] concluded that, at least in the case of benzophenone, it is the ultraviolet absorbed by the ketone which is active. He also found the rate proportional to the intensity of the ultraviolet rather than, as the earlier workers believed, to the square of the visible light intensity. For complete absorption of the available light, the rate, after an induction period of 30 to 60 minutes, reached a steady value inversely proportional to the concentration of oxygen. At 3660A, the quantum yield for oxygen consumed was 18 and the temperature coefficient was 1.7.

Benzoquinone also effects the oxidation of alcohols when irradiated by the wave-lengths 4050, 4080 or 4360A; the quantum yields are unity.[96]

The action of sunlight on the oxidation of alcohols by powdered potassium dichromate[97] produces only aldehydes. With methyl alcohol, the dichromate is reduced to chromic hydroxide and with ethyl alcohol to a brown powder of unknown composition. The ratio of the yield of aldehyde to the quantity of dichromate reduced increases with the time of exposure and reaches after 12 to 24 hours a value of two. With large quantities of dichromate present, the yield of aldehyde drops because of the screening effect of the precipitates formed and of the dichromate itself. Plotnikow,[98] as well as Bowen and co-workers,[99] used the dichromate ion in solution. Plotnikow described a wide variety of photo-öxidations effected by this compound. Ethylene glycol rapidly becomes alkaline and deep green, glycolaldehyde and glyoxal being produced. Glycerol solutions yield glyceric aldehyde and acid and dihydroxyacetone. Propyl alcohol gives propionaldehyde and traces of propionic acid, and isopropyl alcohol acetone and acetic and formic acids. Amyl alcohol yields an aldehyde and a brown precipitate of a chromium chromate.

Bowen emphasized the fact that, although in acid solutions the aldehyde is formed without the production of any chromium precipitate, in neutral solutions there results a precipitate of uncertain composition. In neutral and alkaline solutions, the chromate ion present is photochemically inactive. The quantum efficiency is independent of the light intensity, of added acid (if not too little is present), of temperature and of the dichromate ion concentration between 0.1 and 0.01*N*. Only the ion $HCrO_4^-$ is effective. In strongly alcoholic solutions the quantum yield is approximately one, but in weaker solutions it is diminished.

[94] Boeseken, J., and Langedijk, S. L., *Proc. Acad. Sci. Amsterdam*, **35**, 1124 (1926); Boeseken, J., Cohen, W. D., and Langedijk, S. L., *Rec. trav. Chim.*, **46**, 383 (1927).

[95] Berthoud, A., *Helv. Chim. Acta*, **16**, 592 (1933).

[96] Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 694 (1934); see also work of Leighton and Forbes discussed under actinometers in Chapter 7.

[97] Schwarz, M., *Z. Elektrochem.*, **32**, 15 (1926).

[98] Plotnikow, J., *Chem. Ztg.*, **52**, 669 (1928); Cantieni, R., *Ber.*, **69B**, 2282 (1936) believes the reaction proceeds through a peroxide.

[99] Bowen, E. J., and Bunn, C. W., *J. Chem. Soc.*, 2353 (**1927**); Bowen, E. J., and Yarnold, E. T., *Ibid.*, 1648 (**1929**); Bowen, E. J., Peacocke, T. A., and Wellburn, E. R., *Ibid.*, 1866 (**1931**); Bowen, E. J., and Chatwin, J. E., *Ibid.*, 2081 (**1932**).

With increasing hydrogen ion concentration, the yield increases to a limit of 1.8 for wave-lengths between 4360 and 3665A.[100]

Potassium ferrocyanide solution gives an orange coloration with isobutyl alcohol, especially in light.[101]

Ethers

It has been noted[102] that some samples of commercial ether develop peroxides when exposed to ultraviolet rays and so are unsuitable for use in the tropics, although they satisfy all the usual tests for purity. Irradiation may be employed in testing the stability of various samples. Although Athias[103] believes atmospheric oxygen to be concerned in the decomposition of ether in light, Binz[104] found the photochemical formation of peroxides to be independent of the presence of atmospheric oxygen. Little is known of the nature of the reaction.

In the presence of uranyl nitrate, sunlight is capable of forming oxalic acid from ether, according to Rowell and Russell.[105] They suggest that the light reduces the uranyl to the uranous ion and oxidizes the ether to diglycol, of which part is oxidized to diglycollic acid and part hydrolyzed to glycol, which is further oxidized to oxalic acid.

Milas[106] found the rate of peroxide formation in ethers to depend largely on the type of groups attached to the oxygen atom. Ultraviolet light greatly accelerated the rate of autoxidation of dibenzyl ether in particular.

Acetone photosensitizes dimethyl ether vapor, the rate of decomposition varying with the concentration of the ether, the square root of the absorbed light and inversely as the square root of the acetone concentration.[107] The quantum yields based on carbon monoxide formed were as low as 5 and as high as 230 depending upon the light intensity and total pressure. With diethyl ether, the quantum yields were one-tenth as great under similar conditions.

[100] See also Fugassi, P., *J. Am. Chem. Soc.*, **59**, 2092 (1937).

[101] Kutzlnigg, A., *Z. anal. Chem.*, **77**, 349 (1929); for the action of quinones on alcohols, see Chapter 25.

[102] Liversedge, S. G., *Analyst*, **59**, 815 (1934); *Brit. Chem. Abs.*, **B**, 173 (1935).

[103] Athias, F., *Thesis (Algiers)*, **1924**; *Chim. et ind.*, **14**, 744 (1925); *Chem. Abs.*, **20**, 478 (1926); Matsunami, S., *J. Pharm. Soc. Japan, No.* **520**, 529 (1925); *Chem. Abs.*, **20**, 478 (1926).

[104] Binz, C., *Süddeut. Apoth. Ztg.*, **70**, 128 (1930).

[105] Rowell, S. W., and Russell, A. S., *J. Chem. Soc.*, **127**, 2900 (1925).

[106] Milas, N. A., *J. Am. Chem. Soc.*, **53**, 227 (1931).

[107] Leermakers, J. A., *J. Am. Chem. Soc.*, **56**, 1899 (1934).

Chapter 23

The Behavior of Unsaturated Compounds

The compounds discussed in the preceding chapter have been relatively inert photochemically, reacting (if at all) with low quantum yields, except in the case of sensitized processes or in reactions in which the light is absorbed by some other reactant. It has long been known that in ring compounds the presence of double bonds is usually necessary for marked absorption of the longer ultraviolet wave-lengths. Of the olefinic compounds, ethylene exhibits absorption which begins at 2100A and is nearly complete at 1850-1990A, a region in which ethane exhibits no absorption. The introduction of various substituents in molecules containing a double bond frequently displaces the absorption to longer wave-lengths. Particularly effective is the presence of one or more conjugated double bonds, as Smakula has recently demonstrated.[1]

Several possible types of reactions may follow upon the absorption of light by double bonds. Usually only one of the two carbon-to-carbon linkings is broken. Polymerization may result, two or more of the photochemically produced molecules with free valences combining. In an absorbing compound with substituents on each carbon atom adjacent to the double bond, after absorption of energy has broken one linkage, there may be a rotation about the remaining linking so that when molecules suffer a collision the double bond may be reformed with the production of the stereoisomer of the original compound. More rarely, and particularly when the shorter wave-lengths have been absorbed, the energy is transferred within the molecule to alkyl groups, which may be decomposed with evolution of hydrogen and formation of compounds with triple linkages.

Simple Decompositions

Mooney and Ludlam[2] have shown that ethylene can be decomposed by wave-lengths shorter than 2100A, giving acetylene and hydrogen, together with a small amount of a polymerized product.[3] The long wave-length limit of 2110A corresponds with the heat of dissociation of ethylene into acetylene and hydrogen, 135 kcal. According to McDonald and Norrish,[4] ethylene at low pressures when irradiated in the fluorite region deposits a polymer and forms hydrogen and a condensible gas composed of at least two fractions.

In the presence of excited mercury atoms, ethylene is first slightly decomposed and then the remainder is polymerized.[5] In the presence of hydrogen, ethane is formed, the rate being proportional to the square root of the hydrogen concentration. Taylor and Hill[6] agree that saturated hydrocarbons are formed,

[1] Smakula, A., *Angew. Chemie,* **47,** 657 (1934).
[2] Mooney, R. B., and Ludlam, E. B., *Trans. Faraday Soc.,* **25,** 442 (1929).
[3] Berthelot, D., and Gaudechon, H., *Compt. rend.,* **155,** 207 (1912); Klever, H. W., and Glaser, F., *Mitt. Chem.-tech. Inst. Tech. Hochschule Karlsruhe,* No. **1,** 1 (1922); *Chem. Abs.,* **18,** 1976 (1924).
[4] McDonald, R. D., and Norrish, R. G. W., *Proc. Roy. Soc.,* **157A,** 480 (1936).
[5] Olson, A. R., and Meyers, C. H., *J. Am. Chem. Soc.,* **48,** 389 (1926).
[6] Taylor, H. S., and Hill, D. G., *J. Am. Chem. Soc.,* **51,** 2922 (1929).

but note that they are subsequently decomposed both by the excited mercury atoms and by atomic hydrogen. Methane is the stable product formed in the gas phase and a liquid polymer C_xH_{2x} is deposited on the walls. Jungers and Taylor[7] find the mercury-sensitized hydrogenation more rapid in the case of deuteroethylene than of ethylene. Methane is formed only in negligible amounts, butane being the important product with small amounts of ethane. At low hydrogen concentrations, a photosensitized polymerization occurs; it is slower in the deuterium compound.

In the presence of oxygen, irradiation of ethylene produces some formic acid.[8] In general, in ethylenic and acetylenic compounds in the presence of oxygen, the double and triple linkages are ruptured and simple acids are formed. In the presence of ammonia, cyclic compounds are produced. Ethylene, for example, first yields amino-ethylenes; then ring formation takes place with production of compounds of the pyrrolidine and pyridine types, which may be regarded as the mother substances of alkaloids. According to Milas, Kurz and Anslow,[9] hydrogen peroxide reacts with double-bonded compounds on exposure to ultraviolet light to form glycols, possibly because of a decomposition to two hydroxyl radicals. By this reaction, glycerol, dihydroxybutyric acid, *meso*-tartaric acid and its diethyl ester have been prepared from allyl alcohol, crotonic acid, maleic acid and its diethylester, respectively.

Trichloroethylene undergoes a chlorine-sensitized photo-oxidation at 4360A to dichloroacetyl chloride. It is a chain reaction (quantum yield 40) of zero order with respect to the trichloroethylene and oxygen. The rate is proportional to the absolute intensity of the light absorbed.[10]

Matthews and Elder[11] produce compounds of sulfur dioxide and unsaturated hydrocarbons by direct combination by exposing the mixed liquids to sunlight or ultraviolet rays, or in some cases by heating. The examples given are the compounds with pseudo-butylene $(C_4H_8SO_2)_n$, propylene, amylene and ethylene. The butylene product is a horny or glassy, clear white solid, soluble in chloroform or tetrachloroethane and not easily flammable. It can be used for making varnishes, transparent films, etc., and may be mixed with celluloid by first softening both with acetone. It renders the celluloid less flammable. Work on this reaction has been reviewed by Snow and Frey,[12] who find from their own experiments that the reaction occurs in the liquid phase, the effective wave-length range being 3000 to 3800A. It is catalyzed by oxygen, organic peroxides, hydrogen peroxide, but is inhibited by nitric acid or hydrogen sulfide and is slowed at high temperatures.

Uranium salts sensitize various ethylenic compounds as well as aldehydes to sunlight. Acetylenic compounds react even more readily,[13] aldehyde and formic acid being produced. Amylene yields amyl alcohol. Cyclohexenes, but not cyclohexanes, behave similarly, but benzene does not react in the absence of a side-chain.

The photochemical reduction of sodium dichromate by ethylene glycol has

[7] Jungers, J. C., and Taylor, H. S., *J. Chem. Phys.,* **6,** 325 (1938).
[8] Berthelot, D., and Gaudechon, H., *Compt. rend.,* **150,** 1327 (1910).
[9] Milas, N., Kurz, P. F., and Anslow, W. P., *J. Am. Chem. Soc.,* **59,** 543 (1937).
[10] Müller, K. L., and Schumacher, H. J., *Z. physik. Chem.,* **B37,** 365 (1937).
[11] Matthews, F. E., and Elder, H. M., British P. 11,635, May 11, 1914; Reports Progress Applied Chem., **1,** 192 (1916).
[12] Snow, R. D., and Frey, F. E., *Ind. Eng. Chem.,* **30,** 176 (1938).
[13] Aloy, J., and Valdiguié, A., *Bull. soc. chim.,* **37,** 1135 (1925).

been found to be affected by the presence of water.[14] For equal amounts of light, the ratio of the reductions occurring in one hour with water present and with it absent was 59 to 79. Within the range of 0.2 to 0.6 per cent concentrations of the dichromate in the glycol, the amount of decomposition was proportional to the time.

Reactions in which halogens are added at the double bond are considered in Chapter 28.

Polymerization

Berthelot and Gaudechon[15] observed that ultraviolet rays polymerize ethylene to a liquid having the odor of rancid fat, and boiling below 100°C. According to Taylor and Emeléus,[16] the polymerization of ethylene can be sensitized to the light of the mercury arc by means of ammonia, the rate of the reaction increasing with the ammonia concentration. The formation of saturated hydrocarbons in the reaction system with varied ratios of hydrogen to ethylene is subordinate to the polymerization process. An oil is produced which probably contains the nitrogen of the ammonia decomposed in the process. Emeléus and Taylor[17] found methylamine and ethylamine to induce a similar photopolymerization of ethylene at temperatures above 200°C. Jungers and Taylor[18] find that ethylene cannot be polymerized in quenching the resonance radiation of sodium, possibly because of unfavorable localization of the energy received by the ethylene in the quenching process. It can be induced, however, by the photodecomposition of admixed acetone, due to an effect of radicals from the latter. It is also polymerized by ethyl radicals produced by the mercury-sensitized photodecomposition of ethyl iodide.[19]

Commercial gaseous butadiene, containing 30 per cent pseudobutylene, but not the pure bivinyl gas, is polymerized in the light of the quartz lamp to a white solid, insoluble in alcohol, ether or benzene.[20] Khokhlovkin[21] found a sample of butadiene completely autopolymerized in light (shorter than 2300A) and air at room temperature in 515 days. At 45°C., it occurred in 100 hours. Light considerably increased the rate of the autocatalytic process. Gee[22] finds the quantum yield (0.3) of a mercury-sensitized polymerization nearly independent of the pressure. The main product was an insoluble polymer, with some hydrogen and a cyclic dimer, the latter occurring in greatest proportion at low pressures. 2-Butoxy-1,3-butadiene in ultraviolet light for one week gives 13 per cent of a polymer which is somewhat sticky and elastic.[23]

Ferrer[24] reports that diphenylene ethylene, $(C_6H_4)_2C{:}CH_2$, is stable for several hours in the dark, but is completely polymerized and rendered insoluble in ether, when exposed for ten minutes to the mercury arc.

[14] Riesenfeld, E. H., and Hecht, O., *Z. wiss. Phot.*, **26**, 369 (1929); *Brit. Chem. Abs.*, **1929A**, 895.
[15] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1169 (1910).
[16] Taylor, H. S., and Emeléus, H. J., *J. Am. Chem. Soc.*, **52**, 2150 (1930); **53**, 573 (1931).
[17] Emeléus, H. J., and Taylor, H. S., *J. Am. Chem. Soc.*, **53**, 3370 (1931).
[18] Jungers, J. C., and Taylor, H. S., *J. Chem. Physics*, **4**, 94 (1936); *Chem. Abs.*, **30**, 2109 (1936); *Trans. Faraday Soc.*, **33**, 1353 (1937); *Brit. Chem. Abs.* **A**, 574 (1937).
[19] Joris, G. G., and Jungers, J. C., *Bull. soc. chim. Belg.*, **32**, 4426 (1938); *Chem. Abs.*, **32**, 4426 (1938).
[20] Nikiforov, V. K., and Runtzo, P. M., *Acta Physicochim. U.R.S.S.*, **3**, 335 (1935); *Chem. Abs.*, **30**, 2493 (1936).
[21] Khokhlovkin, M. A., *Sintet Kauchuk, No.* 4, 12 (1936); *Chem. Abs.*, **30**, 6602 (1936); see also Kublitskiĭ, A. M., *Sintet Kauchuk (U.S.S.R.)*, No. 7-8, 30, 1936; *Chem. Abs.*, **31**, 6503 (1937).
[22] Gee, G., *Trans. Faraday Soc.*, **34**, 712 (1938).
[23] Dykstra, H. B., *J. Am. Chem. Soc.*, **57**, 2255 (1935).
[24] Ferrer, J., *Anales soc. espan. fis. quim.*, **20**, 459 (1922); *Chem. Abs.*, **17**, 3177 (1923).

Vinyl chloride and vinyl bromide polymerize rapidly when exposed to light. The chloride forms an amorphous insoluble substance of specific gravity 1.406, which melts above 130°C., with decomposition.[25] The polymerized bromide is likewise insoluble in water, alcohol, or ether, has a specific gravity of 2.075 and begins to decompose at 125 to 130°C. Plotnikow[26] stated the properties of the vinyl chloride polymer, probably $(CH_2CHCl)_{16}$, formed by the extreme ultraviolet rays of a mercury arc, to be those of a "synthetic rubber." Sunlight is effective only in the presence of catalysts, such as the salts of manganese, cobalt, nickel, copper and vanadium and most especially, the uranyl salts. A 2.5-per cent solution of vinyl chloride in methyl alcohol was employed in the apparatus shown in Figure 115. Carbon tetrachloride accelerated the transformation. The white precipitate obtained dissolves in many organic solvents to form colloidal systems varying from paste to solid.

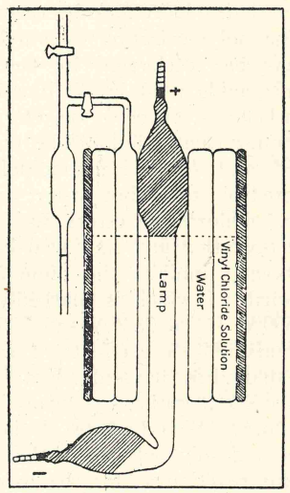


Figure 115.

Apparatus for Synthesizing "Rubber" from Vinyl Chloride. A water-cooled jacket prevents overheating of the vinyl chloride solution.

Courtesy "India Rubber World"

Ostromuislenski[27] obtained by the polymerization of vinyl bromide a material which he termed caouprene bromide. This exists in three forms, called α, β and γ. When the α and β forms are submitted to the action of ultraviolet the γ form is yielded.

It is claimed[28] that if the polymerization of vinyl chloride by sunlight or ultraviolet rays, with or without a catalyst such as a soluble lead salt, is continued beyond the acetone-soluble or α-stage, a new β-modification, insoluble in acetone but soluble in monochlorobenzene, is obtained before conversion into the γ- or δ-forms. The new form may also be obtained from the γ and δ forms by heating them with aniline, quinoline, etc. Monochlorobenzene solutions of the new product to which is added a plasticizer, *e.g.*, a dichlorobenzene, yield flexible, transparent and non-flammable films on drying. The β-product is also obtainable

[25] Baumann, E., *Annalen*, **163**, 317 (1872).
[26] Plotnikow, J., *Z. wiss. Phot.*, **21**, 117 (1922); *Chem. Abs.*, **16**, 1337 (1922).
[27] Ostromuislenski, I., *J. Russ. Phys. Chem. Soc.*, **44**, 204 (1912).
[28] Van Dyk, L. A., British P. 255,837, June 29, 1926; *Brit. Chem. Abs.*, **1927B**, 564.

from the α-compound by prolonged action of ultraviolet rays and heat or by heat alone.[29]

A vinyl halide may also be condensed with a phenol in the presence of aluminum or ferric chloride, before polymerization by ultraviolet light.[30]

According to Guyer and Schütze,[31] 0.1 per cent of hydroquinone prevents the polymerization of vinyl bromide in direct sunlight for several months.

Stobbe and Toepfer[32] report that *p*-vinylanisole is polymerized when placed in glass tubes in direct sunlight, the extent of reaction being about the same after four days' exposure as after four hours at 100°C. in the dark. If a little of the polymeric form is added, the polymerization proceeds as far in one day as it does in four with the pure substance. When *p*-vinylanisole in quartz tubes at 30°C. is alternately irradiated by a quartz mercury lamp and kept dark, polymerization appears not to proceed during the period of raying, but during the following periods of darkness. It is believed that polymerization by rays of wave-lengths longer than 3300A may be reversed by rays of shorter wave-length.

The polymerization of vinyl esters gives rise to various useful products.[33] It may be accelerated by benzoyl peroxide, ozonides, and by anhydrides of organic acids used in conjunction with agents yielding oxygen, as perborates, percarbonates, silver oxide, etc. The polymerization products are solid, colorless and transparent celluloid-like masses which are odorless and can be turned, cut, planed and otherwise manipulated to form various articles. These solids, rendered plastic in hot water, can be molded; upon cooling, the material hardens again. Chlorinated esters may also be polymerized by heat and light in a two-stage operation and employed in lacquers.

Oxygen inhibits the photopolymerization of vinyl acetate, the temperature coefficient of which is markedly greater than unity. The quantum yield is 1.7 at 2300A, 1.2 at 2536A and 936 with a 3000 to 4000A band, indicating a chain mechanism.[34] The effects of various inhibitors in ethyl acetate as solvent have been studied by Jeu and Alyea,[35] who followed the rate of the reaction by measuring the unsaturation by means of Wijs' solution. Among sixteen representative inhibitors, which include alcohols, esters, acids, amines, oximes, phenols, aldehydes and alkaloids, the relative inhibitory power is approximately the same for this reaction as for the oxidation of sodium sulfite. There is, however, no obvious relation to their effects on the photolysis of hydrogen peroxide. Pyrogallol is about 3200 times as effective an inhibitor as is ethyl alcohol.

Groff[36] described a highly plastic composition formed by fluxing on hot differential rolls (100-120°C.) and sheeting out, a mixture of 100 parts vinyl resin (formed by polymerization of 80 parts vinyl chloride and 20 parts vinyl acetate), 60 parts ethylene glycol monoethyl ether diester of ethylene glycol phthalate, 1 part carnauba wax, 1 part calcium stearate and 1 part calcium hydroxide. Exposure for 100 hours to radiation from a mercury arc at a distance of 20 inches caused only a slight discoloration and did not affect the flexibility.

Vinylethinylcarbinols may be polymerized by the action of air, light or both;

[29] Van Dyk, L. A., British P. 260,550, July 26, 1926; *Brit. Chem. Abs.*, **1927B,** 564.

[30] British Celanese, Ltd., British P. 409,132, April 18, 1933; *Brit. Chem. Abs.* **B,** 534 (1934).

[31] Guyer, A., and Schütze, H., *Helv. Chim. Acta,* **17,** 1544 (1934).

[32] Stobbe, H., and Toepfer, K., *Ber.*, **57B,** 484 (1924); *Chem. Abs.*, **18,** 2503 (1924).

[33] Klatte, F., and Rollett, A., U. S. P. 1,241,738, Oct. 2, 1917; *cf.* Kuhl, H., *Reports of the Progress of Applied Chemistry, Soc. Chem. Ind.*, **1,** 192 (1916); *J. Soc. Chem. Ind.*, **34,** 623 (1915).

[34] Vernon, A. A., and Taylor, H. S., *J. Am. Chem. Soc.*, **53,** 2537 (1931).

[35] Jeu, K-K., and Alyea, H. N., *J. Am. Chem. Soc.*, **55,** 575 (1933).

[36] **Groff, F.,** U. S. P. 1,966,856, July 17, 1934, to Carbide and Carbon Chemicals Corp.

the process is accelerated by the use of halides such as those of zinc, iron, aluminum, antimony, bismuth, boron and tin, organic peroxides such as benzoyl peroxides or acetyl peroxide, ozone, hydrogen peroxide or persalts, or by accelerators of the photochemical reaction such as uranyl nitrate.[37] Products of various consistencies and solubilities are obtained, suitable for use in coating compositions, manufacture of safety glass, impregnation of paper or cloth, or in compositions for molding, etc.

Dreyfus[38] describes the polymerization of vinyl compounds containing hydrophile groups, as hydroxyl, carboxyl, sulfonic acid, amino or other acid or basic groups, which render them more readily soluble or dispersible in aqueous liquids. Vinyl chloride is heated to 80° to 100°C. in an autoclave with sodium glycol to produce glycolmonovinyl ether; this product may be polymerized by warming with benzoyl peroxide and under the radiation from a quartz mercury-vapor lamp. The polymerized product may be dissolved in water and used directly as a size.[39]

The polymerization of vinyl chloride by heating with a small proportion of benzoyl peroxide at about 50° to 60°C. for 24 hours may be assisted by a preliminary exposure of the initial material in the gaseous state to rays from a mercury lamp.[40] Voss and Dickhäuser[41] obtain products resembling celluloid by gradually heating a vinyl halide under pressure to a temperature preferably not above 100°C. The halide may be irradiated, and an inert or a polymerizable organic solvent, such as benzene or butadiene, and a catalyst such as benzoyl peroxide may be present.[42]

Shmidt states that the powdery product obtained by polymerization of vinyl chloride without a solvent is converted into a colorless, glass-like mass on prolonged exposure to the light of a quartz mercury arc.[43]

The polymerization of vinyl derivatives of phenols or cresols may be conducted in the presence of anhydrous aluminum chloride or ferric chloride as condensing agents by the action of ultraviolet light or heat.[44] Pressure polymerization is used in the preparation of resins from vinyl chloride by Waterman, Leendertse and Colthoff.[45] Although polyvinyl chloride has poor light stability,[46] glass laminated with a vinyl resin showed no discoloration after exposure for a thousand hours to the Uviarc or after two years in Florida.[47]

[37] Carothers, W. H., Berchet, G. J., and Jacobson, R. A., U. S. P. 1,963,074, June 19, 1934, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, **28,** 4848 (1934).

[38] Dreyfus, H., British P. 398,173, Sept. 1, 1933; *Chem. Abs.*, **28,** 1360 (1934).

[39] Note also Zhukov, I., Komarov, V. A., and Sibiryakova, G. N., *Colloid J. (U.S.S.R.)*, **1,** 9 (1935) for bivinyl polymers. For the effects of light on the oxidation rates of 1,1,5,5-tetraphenyl-1,4-pentadiene and 1,1,6,6-tetraphenyl-1,5-hexadiene, see Bauer, K. H., and Herzog, H., *J. prakt. Chem.*, **147,** 4 (1936).

[40] Klatte, F., and Müller, H., U. S. P. 1,920,403, Aug. 1, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **27,** 4816 (1933).

[41] Voss, A., and Dickhäuser, E., German P. 579,048, June 20, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **27,** 4943 (1933); see also British P. 294,474, July 23, 1927, in which vinyl esters are polymerized under ultraviolet to make rubber substitutes, proteins, peptones or amino-acids being added to impart elasticity.

[42] British P. 385,004, Dec. 22, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **27,** 4251 (1933).

[43] Shmidt, Y., *Org. Chem. Ind. (U.S.S.R.)*, **5,** 116 (1938); *Chem. Abs.*, **32,** 5957 (1938).

[44] British P. 409,132, April 26, 1934, to British Celanese, Ltd.; *Chem. Abs.*, **28,** 6158 (1934).

[45] Waterman, H. I., Leendertse, J. J., and Colthoff, P. J. G., *Chem. Weekblad*, **32,** 550 (1935); *Chem. Abs.*, **30,** 1147 (1936); Blackie, K. G., and Crozier, R. N., *Ind. Eng. Chem.*, **28,** 1155 (1936). See also Plauson, H., U. S. P. 2,127,135, Aug. 16, 1938; *Chem. Abs.*, **32,** 8043 (1938) for vinyl acetate polymerization by light when emulsified with sulfonated castor oil.

[46] Curme, G. O., Jr., and Douglas, S. D., *Ind. Eng. Chem.*, **28,** 1123 (1936).

[47] Sherts, J. H., and Fix, E. L., *Chem. Met. Eng.*, **43,** 177 (1936). Of a series of synthetic plastics tested for suitability for flexible windshield material for aircraft, cellulose acetobutyrate and vinyl acetate resins showed the greatest resistance to discoloration by ultraviolet light, but had certain disadvantages. Axilrod, B. M., and Kline, G. M., *J. Res. Bureau of Standards*, **19,** 367 (1937).

[48] Duggan, F. W., U. S. P. 2,126,179, Aug. 9, 1938; *Chem. Abs.*, **32,** 7610 (1938).

For stabilizing vinyl resins to light, Duggan uses one to five per cent of butyl salicylate or other phenol derivative with a single hydroxyl group and an alkyl-substituted carboxyl group ortho to the hydroxyl group.[48]

Stereoisomeric Transformation

The *trans*-isomer has a greater ultraviolet absorption than the *cis*-form in many compounds, including: ClCH=CHCl, C_2H_5CH=CHBr, CH_3CH=CHBr, ClCH=CHI, and fumaric acid.[49]

The difference between the absorption curves of the geometrical isomers increases with decreasing wave-length. Compounds containing iodine differ in that this relation is inverted at wave-lengths greater than 3000A, the *cis* form absorbing more in this region than the *trans* form. The inversion may be due in some manner to the liberation of free iodine.[50]

According to van de Walle and Henne,[51] if either the *cis* or *trans* isomer of chloroiodoethylene is exposed to sunlight for one hour, the same equilibrium mixture (which contains 17.5 per cent of the *trans* form) is obtained. The theory underlying the conversion of geometrical isomers has been discussed by Olson [52] and by Mulliken,[53] and studies of the process were made in aqueous solutions of various fumaric and maleic acids by Olson and Hudson,[54] who reviewed the earlier experimental work. It is suggested that in the normal state the carbon atoms of the unsaturated compounds are to be regarded as two tetrahedra joined along a common edge. On excitation by light, they may be considered as joined only at one corner. Rotation about this corner with inversion of one of the carbon atoms will account for the occurrence of a transition between optical isomers if it occurs before a collision removes the energy of excitation and restores a normal state in which the double bond is present. Besides the theory of free rotation in the upper electronic state, Olson discussed the possibility of the addition of an atom or free radical to the face of the carbon tetrahedron, followed by the simultaneous ejection of another group accompanied by isomerization.[55]

The probability p that a molecule in an excited electronic state will return to the *trans* state on deactivation bears to the probability that it will yield the *cis* form $(1-p)$ the ratio given by

$$\frac{p}{1-p} = \frac{C_{Tr}}{C_{Cis}} \times \frac{\epsilon_{Tr}}{\epsilon_{Cis}}$$

in which ϵ_{Tr} and ϵ_{Cis} are the extinction coefficients for the monochromatic light employed and C_{Tr} and C_{Cis} are the mole percentages of the *trans* and *cis* isomers. It was possible to test the relation in the gas state in the case of the isomers of dichloroethylene and dibromoethylene. Agreement with the theory was attained for the stationary states set up at various temperatures, the proportion of the two isomers present being determined by dielectric constant measurements. Further

[49] Errera, J., and Henri, V., *Compt. rend.*, **180**, 2049 (1925); **181**, 548 (1925). Errera, J., *J. phys. Radium*, **7**, 215 (1926).

[50] See also Kirrmann, A., and Volkringer, H., *Compt. rend.*, **182**, 1468 (1926); Ramart-Lucas, Mme., *Compt. rend.*, **188**, 638, 1301; **189**, 802 (1929); *Bull. soc. chim.*, **51**, 965 (1932); Bourguel, M., Gredy, B., and Piaux, L., *Compt. rend.*, **195**, 129 (1932).

[51] Van de Walle, H., and Henne, A., *Bull. sci. acad. roy. Belg.*, **11**, 360 (1925); *Chem. Abs.*, **20**, 1049 (1926).

[52] Olson, A. R., *Trans. Faraday Soc.*, **27**, 69 (1931).

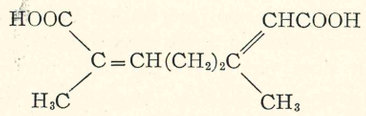
[53] Mulliken, R. S., *Phys. Rev.*, **41**, 751 (1932).

[54] Olson, A. R., and Hudson, F. L., *J. Am. Chem. Soc.*, **55**, 1410 (1933).

[55] Olson, A. R., *J. Chem. Physics*, **1**, 418 (1933).

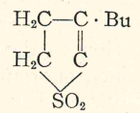
studies in the case of the chlorine compounds have been reported by Mahncke and Noyes.[56] There are three absorption regions: (1) continuous, by the carbon-chlorine bond from about 2500A with maxima at 1950A for the *cis* and 1850A for the *trans* form; (2) bands beginning at about 1540A, and (3) another continuous region extending down to 750A. In the first absorption region, produced by irradiation with an aluminum spark, atomic chlorine appears to be formed, with possibly some hydrogen chloride. For this reason, Olson's second theory is favored when the change is induced by light in this region of the spectrum. *cis*-Dichloroethylene also yields small amounts of a solid polymerization product, melting at 103.5° to 104°C. These observations have also been confirmed by Müller and Ehrmann.[57]

The compound



undergoes a *cis-trans* isomerization in ultraviolet light to a more soluble form.[58]

Other Types of Isomerization. The isomerization of the sulfones of β-alkyl-butadienes in alkaline solution under the influence of ultraviolet light consists in a displacement of the double linking in the ring toward the alkyl.[59] *Tert*-butyl-butadienesulfone is isomerized to a compound



The isomer of the sulfone of 2-phenyl-1,3-butadiene and ozone when irradiated gave propiophenonesulfonic acid, showing that the change was not a *cis-trans* isomerism, as believed by Eigenberger [60] to occur in the irradiation of isoprene sulfone in the presence of alkali.

The homologs of isoprenesulfone isomerize on exposure to ultraviolet,[61] the change involving a wandering of the double bond.

According to Sherrill, Otto and Pickett,[62] sunlight and ultraviolet light of shorter wave-lengths transform 2-pentene into an isomeric form with slightly different physical properties. The transformed product adds hydrogen bromide to form 15 per cent of 3-bromopentane and 85 per cent of 2-bromopentane.[63] Birch and Stansfield [64] note that ultraviolet light favors the formation of a peroxide in cyclohexene.

[56] Mahncke, H. E., and Noyes, W. A., Jr., *J. Chem. Physics*, **3**, 536 (1935); *J. Am. Chem. Soc.*, **58**, 932 (1936).

[57] Müller, E., and Ehrmann, K., *Ber.*, **69B**, 2207 (1936). See also Stockmann, H., and Stoermer, R., [*Ber.*, **47**, 1793 (1914)] for work on γ-phenylvinylacetic acid in benzene solution.

[58] Kuhn, R., Köhler, L., and Köhler, F., *Z. physiol. Chem.*, **242**, 171 (1936).

[59] Backer, H. J., and Strating, J., *Rec. trav. chim.*, **54**, 170, 618 (1935); *Chem. Abs.*, **29**, 2959 (1935); **30**, 3403 (1936).

[60] Eigenberger, E., *J. prakt. Chem.*, **129**, 312 (1931); *Chem. Abs.*, **25**, 2969 (1931); see also van Zuydewijn, E. de R., *Rec. trav. chim.*, **56**, 1047 (1937).

[61] Backer, H. J., and Strating, J., *Rec. trav. chim.*, **53**, 525 (1934); Backer, H. J., Strating, J., and Zuithoff, A. J., *Ibid.*, **55**, 761 (1936).

[62] Sherrill, M. L., Otto, B., and Pickett, L. W., *J. Am. Chem. Soc.*, **51**, 3032 (1929).

[63] For the ultraviolet absorption spectra of the various isomeric 2-pentenes, Carr, E. P., *J. Am. Chem. Soc.*, **51**, 3041 (1929).

[64] Birch, S. F., and Stansfield, R., *Nature*, **123**, 490 (1929).

Acetylene. The pure gas exhibits a banded absorption spectrum which begins at 2400A according to Kistiakowsky,[65] or at 2300A according to Hopfield,[66] or at lower pressures (less than 30 mm.) at 2070A.[67] A second system begins at about 1540A and at higher pressures a continuous absorption appears to set in at about 1880A, but may be due to an impurity.[68] Jonescu gives an extrapolated heat of dissociation of 204 kcal. Kato,[69] however, claims to have noted on the vaporization of solid acetylene at room temperatures, a broad continuous absorption spectrum and some series of bands with fine structure. The former, showing its strongest absorption at 2560 and 2400A, is held to indicate predissociation. The latter, appearing below 2500A, is attributed to deformation vibrations.

Berthelot and Gaudechon[70] found exposure of acetylene to the action of ultraviolet rays to bring about a partial polymerization to a yellow solid, but no decomposition. No benzene was found in these experiments.

Daylight or sunlight does not affect carefully purified and dried acetylene, but with wave-lengths less than 3000A, the reaction occurs at atmospheric or higher pressures and at room temperature, giving the yellow product without any separation of carbon.[71] The process is disturbed by the presence of oxygen or moisture, the latter leading to the formation of aldehyde. The wave-length limit was set at 2537A or less by Lind and Livingston,[72] who found the rate of polymerization to be proportional to the intensity of the absorbed light but independent otherwise of the acetylene pressure. The temperature coefficient was 1.25, and the quantum yield appeared to be 9.2 for the wave-length 2150A. This value was somewhat uncertain since measurements had to be limited to the beginning of the reaction owing to the deposition of the polymer on the walls of the vessel. The solid product, cuprene or a very similar substance, had the empirical formula $(C_{10}H_9)_n$. Some benzene formation was observed and could be accounted for by side reactions. Kato confirmed the formation of both cuprene and benzene by the wave-lengths 2103, 2100.5, 2065, 2036 and 2026A, but believed 2200A to produce chiefly benzene. At higher temperatures, 270° to 376°C., both he and Livingston and Schiflett[73] found benzene to predominate; the latter workers observed that two nonvolatile solids and a yellow, viscous, voltatile liquid were also produced. By following the absorption changes during the polymerization of acetylene, Kemula and Mrazek[74] detected the formation not only of benzene, but of naphthalene as well, together with less than 0.25 per cent of ethylene and ethane, but no hydrogen in the gas phase. Bates and Taylor[75] noted that polymerization could also be effected by excited mercury atoms, but that acetylene could not be hydrogenated by hydrogen which had been activated by excited mercury vapor.

[65] Kistiakowsky, G. B., *Phys. Rev.*, **37**, 276 (1931).
[66] Hopfield, J. J., *Phys. Rev.*, **29**, 356 (1927).
[67] Herzberg, G., *Trans. Faraday Soc.*, **27**, 379 (1931).
[68] For data on the classification of the bands, see Price, W. C., *Phys. Rev.*, **45**, 843 (1934); Jonescu, A., *Compt. rend.*, **199**, 710 (1934); Woo, S.-C., Liu, T.-K., Chu, T. C., and Chih, W., *J. Chem. Phys.*, **6**, 240 (1938).
[69] Kato, S., *Bull. Inst. Phys.-Chem. Research (Tokyo)*, **10**, 343 (1931); *Chem. Abs.*, **25**, 5845 (1935).
[70] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1169 (1910); **151**, 395 (1910); **155**, 521 (1912).
[71] Reinicke, H., *Z. angew. Chem.*, **41**, 1144 (1928).
[72] Lind, S. C., and Livingston, R., *J. Am. Chem. Soc.*, **52**, 4613 (1930); **54**, 94 (1932).
[73] Livingston, R., and Schiflett, C. H., *J. Phys. Chem.*, **38**, 377 (1934); see also Ch. Rosenblum, *Bull. soc. chim. Belg.*, **46**, 503 (1937); *Chem. Abs.*, **32**, 2840 (1938).
[74] Kemula, W., and Mrazek, S., *Z. physik. Chem.*, **23B**, 358 (1933).
[75] Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, **49**, 2438 (1927).

Toul[76] believed polymerization in the presence of mercury vapor should not be considered a true photosensitization since it can still be observed when a source is used which does not emit the lines which excite mercury. The adddition of 0.006 per cent of oxygen did not affect the reaction. He also believed that an equilibrium was reached with the polymer after the volume had been reduced by 10 per cent, but this result could not be duplicated by Kemula.[77] Melville[78] treats the process as a sensitized chain reaction in which the excited mercury atoms form with the acetylene molecule a complex which successively builds up. The chain length is independent of the acetylene pressure, or surface, or of the rate at which the chains are started and may at 250°C. attain a maximum of 100. Cessation of growth is attributed to a special type of collision of the growing polymer with an acetylene molecule. Jungers and Taylor[79] found the rate of this photosensitized reaction to be 30 per cent greater with acetylene than with heavy-hydrogen acetylene. They gave the quantum yield as 6.5 for acetylene and 5 for acetylene-D_2.

Both methylacetylene and its double-bonded isomer allene can also be polymerized to white solids by ultraviolet radiation,[80] the quantum yields being 3.5 and 2.5, respectively. Diacetylene can also be polymerized.[81]

The photochemical oxidation of acetylene yields oxalic acid and a trace of aldehyde.[82] A mechanism was suggested by Mecke[83] according to which an excited acetylene molecule adds directly to an oxygen molecule. Livingston notes that further oxidation of the resulting glyoxal would account for the formation of the oxalic acid. It is also possible that two molecules of oxygen might be added to the excited acetylene molecule, the double peroxide then rearranging to oxalic acid. In the presence of water vapor in the gas phase in the absence of oxygen or in an aqueous solution, Livingston and Schiflett[84] could detect neither the formation of aldehydes nor ketones.

Heinemann[85] claims to secure the union of acetylene and methane by heating these gases or irradiating them with ultraviolet rays, in the presence of such catalytic metals as iron, nickel, copper, silver, iridium or platinum.

Carothers[86] finds the addition of thio-*p*-cresol to divinylacetylene $CH_2{=}CH{\equiv}CH{=}CH_2$ to be powerfully accelerated by the light of a mercury arc transmitted through soda-glass.

Polymerization of 1-chloro, 1-bromo- and 1-iodo-2-vinylacetylene to form resinous solids may be accelerated by the use of ultraviolet light, benzoyl peroxides, ozonides, etc. The iodine and bromine polymers are very explosive, and the chlorine derivative less so.[87]

Aldehydes and Ketones.[88] *Absorption.* These compounds in the gaseous

[76] Toul, F., *Coll. Czech. Chem. Comm.*, **6**, 162 (1934); *Brit. Chem. Abs.*, **A**, 852 (1934).
[77] Kemula, W., *Coll. Czech. Chem. Comm.*, **7**, 319, 491, 493 (1935); *Chem. Abs.*, **29**, 7775 (1935); **30**, 1644 (1936).
[78] Melville, H. W., *Trans. Faraday Soc.*, **32**, 258 (1936).
[79] Jungers, J. C., and Taylor, H. S., *J. Chem. Physics*, **3**, 338 (1935).
[80] Lind, S. C., and Livingston, R., *J. Am. Chem. Soc.*, **55**, 1036 (1933).
[81] Müller, F. G., and Bänninger, A., *Helv. Chim. Acta*, **10**, 763 (1927).
[82] Livingston, R., *J. Am. Chem. Soc.*, **53**, 3909 (1931).
[83] Mecke, R., *Trans. Faraday Soc.*, **27**, 374 (1931).
[84] Livingston, R., and Schiflett, C. H., *J. Phys. Chem.*, **36**, 750 (1932).
[85] Heinemann, A., U. S. P. 1,202,385, Oct. 24, 1916; 1,134,667, Apr. 7, 1915.
[86] Carothers, W., *J. Am. Chem. Soc.*, **55**, 2008 (1933).
[87] Jacobson, R. A., U. S. P. 1,967,864, July 24, 1934; *Chem. Abs.*, **28**, 5834 (1934).
[88] For a recent review, see Leighton, P. A., *J. Phys. Chem.*, **42**, 749 (1938).

state exhibit a broad absorption band attributed to the carbonyl group and having its maximum at about 2900 to 2800A.[89]

In hexane solutions, the absorption is in general similar. Formaldehyde, for example, either as vapor or in hexane at −70°, exhibits absorption chiefly between 3542 and 2750A, the maximum being at 2940A in hexane and at 2935A in the vapor.[90] Acetaldehyde and propionaldehyde behave similarly. Data on hexane solutions of higher aldehydes through octylaldehyde have been given by Conrad-Billroth.[91]

In water, however, the absorption of the three lowest aldehydes is somewhat displaced toward shorter wave-lengths, the maximum being at 2800A. The formation of hydrates also decreases the absorption. Choral hydrate lacks the typical aldehyde absorption band. The same is true of methylal and acetal.[92] Schou believes that in aqueous formaldehyde solutions there is less than one molecule of formaldehyde for 1200 molecules of the hydrated or polymerized form. Under certain conditions (the presence of a trace of alkali or after polymerization by acid) acetaldehyde gives spectral evidence that some of the molecules are present in enolic form.[93] This may be detected by a study of the absorption coefficients near the minimum close to 2400A. Herold and Wolf[94] find that propionaldehyde in water forms an association complex and a hydrate which do not absorb in the same region as the carbonyl group. In propyl alcohol as solvent, absorption measurements indicate that the greatest part of the aldehyde has been converted to the half-acetal.[95]

Interpretations of the absorption spectra of formaldehyde vapor have been given by Henri and Schou,[96] by Herzberg,[97] and by Dieke and Kistiakowsky.[98]

Observations in the far ultraviolet at 1750 to 1150A have been reported by Price.[99] About 32 bands are distinguished between 3550 and 2500A. Those on the longer wave-length side contain rotational fine structure but become diffuse, indicating predissociation, at about 2670A to 2750A. This limit is shifted toward the red at higher temperatures.

Reactions. Berthelot and Gaudechon[100] showed that ultraviolet light decomposes formaldehyde vapor with the production of carbon monoxide and hydrogen but no carbon dioxide. Some polymerization also occurred. Bredig and von Goldberger, however[101] claimed to have detected small amounts of carbon dioxide and methane, but Norrish and Kirkbride[102] were unable to verify these results. They

[89] Purvis, J. E., and McCleland, N. P., *J. Chem. Soc.*, **103**, 433 (1913); Bielecki, J., and Henri, V., *Ber.*, **45**, 2819 (1912); Purvis, J. E., *J. Chem. Soc.*, **127**, 9 (1925); Eastwood, E., and Snow, C. P., *Nature*, **133**, 908 (1934).

[90] Schou, S. A., *Compt. rend.*, **186**, 690 (1928).

[91] Conrad-Billroth, H., *Z. physik. Chem.*, **B23**, 315 (1933).

[92] Schou, S. A., *Compt. rend.*, **182**, 965 (1926); *J. chim. phys.*, **26**, 69 (1929).

[93] See also Kwiecinski, L., and Marchlewski, L., *Bull. soc. chim.*, **45**, 591 (1929).

[94] Herold, W., and Wolf, K. L., *Z. physik. Chem.*, **B12**, 165 (1931); *Z. Elektrochem.*, **39**, 566 (1933).

[95] See also Backès, M., *Compt. rend.*, **200**, 1669 (1935).

[96] Henri, V., and Schou, S. A., *Nature*, **118**, 225 (1926); *Z. Physik*, **49**, 774 (1928); *J. chim. phys.*, **25**, 665 (1928); *Compt. rend.*, **182**, 1612 (1926); **186**, 1050 (1928); **199**, 849 (1934).

[97] Herzberg, G., *Trans. Faraday Soc.*, **27**, 378 (1931).

[98] Dieke, G. H., and Kistiakowsky, G. B., *Phys. Rev.*, **45**, 4 (1934); *Proc. Nat. Acad. Sci.*, **18**, 367 (1932). See also Kato, S., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **23**, 256 (1934); *Chem. Abs.*, **28**, 4312 (1934).

[99] Price, W. C., *Phys. Rev.*, **46**, 529 (1934).

[100] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151**, 478 (1910).

[101] Bredig, G., and von Goldberger, A., *Z. physik. Chem.*, **110**, 521 (1924); see also Frank, A., and Pollitzer, E., *Monatsh.*, **34**, 797 (1913).

[102] Norrish, R. G. W., and Kirkbride, F. W., *J. Chem. Soc.*, **135**, 1518 (1932); *Trans. Faraday Soc.*, **27**, 404 (1931).

show from the nature of the products and from energetic considerations that, although the light is absorbed by the carbonyl group, the primary dissociation does not yield a CH_2 group and an oxygen atom. Instead, CO is thought to be removed bodily, the hydrogen atoms combining without first separating from the molecule.

$$\begin{matrix} H \\ H \end{matrix} > CO + h\nu \longrightarrow H_2 + CO$$

This view was based upon what was then known of the behavior of other aldehydes and ketones. If ketones with two different alkyl groups should produce free radicals in the primary process, a mixture of hydrocarbons might be expected as a result of the photochemical decomposition. Actually, it appeared that only one hydrocarbon resulted. Should a free methyl radical be produced from acetaldehyde in the primary process, one might expect ethane as well as methane. This was not observed. Furthermore, a primary process involving free radicals might give rise to a short chain reaction, the free radicals reacting with an additional molecule of the original aldehyde or ketone. Bowen and Watts[103] did, indeed, find a quantum yield of two for the decomposition of acetaldehyde, but it seemed that the occurrence of a complicating polymerization made these results not very accurate. Norrish and Kirkbride therefore proposed as a general mechanism for the primary process in the decomposition of aldehydes and ketones, the elimination of CO, the remaining radicals combining without first separating from the molecule. Subsequent work has shown, however, that other processes must also be admitted. See, for example, the discussion of acetone.

The formaldehyde decomposition can be made to proceed by wave-lengths corresponding to the region of rotational fine structure, that is, by wave-lengths longer than those which cause predissociation. The quantum yield was 1.1 at 3030 to 3130A or 0.7 at 3340 to 3650A. In the predissociation region the quantum yield was 0.9 (2540-2650A).

Later, Patat[104] found that the addition of oxygen produced no change in the ratio of hydrogen to carbon monoxide produced by irradiating formaldehyde vapor within the fine structure region longer than 3000A and uncomplicated by an underlying continuum. From this it was concluded[105] that no hydrogen atoms are there produced. Patat showed the same to be true of the reaction conducted in part of the predissociation region (3000-2700A), thus supporting the Norrish mechanism. The presence of free hydrogen atoms could, however, be detected by this method when the irradiation was made in the region of continuous absorption.

The primary process advanced by Mecke[106] and by Herzberg[107] involved a dissociation in the predissociation region into H and HCO. This was assumed to require 92 kcal., the energy of the 2750A line being 105 kcal. Norrish and Patat each gave reasons for believing that this is not the actual process at the longer-wave portions of the predissociation region. Patat suggests that molecular thermal vibrations may contribute part of the energy required for the simultaneous breaking of two C—H bonds, which must occur since hydrogen atoms are not detected.

Experiments by Norrish and Noyes with radiations in the Schumann region gave no evidence for the formation of oxygen atoms and CH_2 in the primary process, due probably to wave-lengths shorter than 1600A. The final products were the same as those produced by longer wave-lengths in the near ultraviolet.[108]

[103] Bowen, E. J., and Watts, H. G., *J. Chem. Soc.*, **129**, 1607 (1926).

[104] Patat, F., *Z. physik. Chem.*, **25B**, 208 (1934).

[105] Patat, F., and Löcker, T., *Z. physik. Chem.*, **27B**, 431 (1934).

[106] Mecke, R., *Nature*, **125**, 526 (1930).

[107] Herzberg, G., *Trans. Faraday Soc.*, **27**, 383 (1931).

[108] Norrish, R. G. W., and Noyes, W. A., Jr., *Proc. Roy. Soc.*, **A163**, 221 (1937).

Before considering the photolysis of other aldehydes, a few other reactions of formaldehyde may be briefly mentioned. Ghosh and Nandy[109] found its oxidation by hydrogen peroxide in acid solution with a tungstic acid sol as photosensitizer, to be unimolecular with respect to hydrogen peroxide at low concentrations. It tended to become of zero order at higher ones. For low concentrations of free hydrochloric acid, the velocity coefficient varies as the square root of the intensity of the incident radiation, but the variation of the velocity with the intensity of the light is much less at higher acid concentrations. The quantum efficiency of the reaction is between two and seven.

In a reaction between chlorine and formaldehyde, the final products are carbon monoxide and hydrogen chloride. By an analysis of the curves giving the change of pressure with time of irradiation, Krauskopf and Rollefson,[110] who used mixtures of the reactants in various proportions, concluded two reactions to be involved. The first, a very rapid reaction, involved the formation of a new intermediate compound, formyl chloride, produced together with hydrogen chloride by the action of chlorine atoms, formed in the primary photochemical process, upon formaldehyde. This then reacted more slowly in a secondary reaction, which might be either a thermal or a sensitized photochemical reaction, to yield carbon monoxide and hydrogen chloride. This decomposition appeared to be a heterogeneous surface reaction. Under certain conditions, the first reaction proceeded with explosive rapidity. The overall reaction had a quantum yield of about 10^4, and was very susceptible to the action of such inhibitors as oxygen or mercuric chloride. Side reactions, such as the polymerization or decomposition of formaldehyde, the formation of phosgene, or one between hydrogen chloride and formaldehyde, were so slow as to be negligible.

Roman[111] claims to convert such aldehydes as formaldehyde into alcohols by the action of luminous energy from which harmful radiations have been filtered.

Acetaldehyde. Acetaldehyde is also partly polymerized and partly decomposed into methane and carbon monoxide in ultraviolet light,[112] even that of sunlight. In some experiments of Berthelot and Gaudechon particularly with extreme ultraviolet rays, it was observed that the proportion of methane to carbon monoxide was somewhat less than exactly that corresponding to a simple decomposition. This was assumed to be due to a polymerization of the acetaldehyde in part to paraldehyde which was then photolyzed to carbon monoxide and ethane or more complex substances. Radiations of wave-length 2500A caused a rapid polymerization, both paraldehyde and metaldehyde being formed. The presence of water checked these processes, but favored the formation of formic acid. It was also believed that even in the absence of oxygen, a portion of the aldehyde was oxidized to acetic acid.

By comparison with a uranyl oxalate actinometer the quantum yield of which was taken as one, Bowen and Watts[113] concluded that in the unsaturated vapor of acetaldehyde, the quantum yield for polymerization is 1.6 and for decomposition 0.4. The use of the more accurate value of 0.55 for the quantum yield of the actinometer found by Leighton and Forbes[114] makes these values 0.88 and 0.22, respectively.

The absorption of acetaldehyde extends from about 3480 to 2300A, with a maximum at about 2890A, the absorption falling off on either side, according to Smith.[115] Bands with distinct rotational structure set in faintly at 3484A and extend to about 3300A, below which the structure gradually becomes more diffuse and disappears because of predissociation near 3080A. From this wave-length, however,

[109] Ghosh, J. C., and Nandy, S. K., *J. Indian Chem. Soc.*, **6**, 975 (1929); *Chem. Abs.*, **24**, 2055 (1930).
[110] Krauskopf, K. B., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 2542 (1934).
[111] Roman, L. H., French P. 734,065, July 19, 1930; *Chem. Abs.*, **27**, 992 (1933).
[112] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 68, 233 (1913).
[113] Bowen, E. J., and Watts, H. G., *J. Chem. Soc.*, 1607 (**1926**).
[114] Leighton, W., and Forbes, G. S., *J. Am. Chem. Soc.*, **52**, 3139 (1930).
[115] Smith, J. H. C., *Carnegie Inst. Reports*, **27**, 178 (1928).

about 60 diffuse bands continue to 2820A.[116] According to Leighton and Blacet[117] these diffuse bands extend even further to 2730A, and traces can be detected even at 2660A. There is also, underlying the banded absorption, a broad continuous absorption, which begins at about 3080, that is, in the region where the bands still show some rotational fine structure; it has a maximum at 2750A. The greatest total absorption (bands plus continuum) occurs at 1890A.[118]

Using the total radiation from a mercury arc, Smith[119] found the rate of the decomposition of acetaldehyde vapor to be independent of pressure and directly proportional to the intensity of the incident light. That of polymerization was directly proportional to pressure and proportional to the logarithm of the light intensity. Smith found that decomposition is produced chiefly by the shorter wave-lengths, and that polymerization could be produced throughout the absorption band with an estimated quantum yield of only 0.04 for an average wave-length of 2650A.

Leighton and Blacet in general confirmed the observations of Smith on the relative predominance of the two types of reactions at various wave-length regions by careful studies of the quantum yields of each at several pressures in the fine structure, predissociation and predominantly continuous regions. Fluorescence of the aldehyde vapor could be observed between 3342 and 2804A, but not at shorter wave-lengths. Because of this, it was suggested that a mechanism involving activated molecules must apply in these regions and be concerned with polymerization. It was found that the yield for the polymerization reaction at a pressure of 200 mm. dropped from 0.47 at 3130A to only 0.1 at 2537A in the region of continuous absorption. Conversely, the yields for decomposition were 0.2 and 0.9 under these conditions. At 3130A there is considerable fluorescence, the bands are not altogether without fine structure and the amount of continuous absorption is small. Here the yield of polymerization increases with the pressure from 0.266 at 14 mm. to 0.638 at 291 mm. The yield for decomposition decreases from 0.396 at 14 mm. to 0.193 at 291 mm. This decrease was attributed to a removal of activated molecules, which were believed also to contribute to the process of dissociation. The mechanism suggested for the observations in this wave-length region were analogous to those of Norrish for the decomposition of formaldehyde in its long wave-length region.

$$\mathrm{RCHO} + h\nu \longrightarrow \mathrm{RCHO}^*$$
$$\mathrm{RCHO}^* + \mathrm{RCHO} \longrightarrow (\mathrm{RHCO})_2, \text{ etc. for polymerization.}$$
$$\mathrm{RHCO}^* \longrightarrow \mathrm{RHCO} + h\nu' \text{ (fluorescence.)}$$
$$\mathrm{RCHO}^* + \mathrm{M} \longrightarrow \mathrm{RHCO} + \mathrm{M}\,(\mathrm{K.E.}) \text{ (deactivating collisions)}$$
$$\mathrm{RHCO}^* + \mathrm{M} \longrightarrow \mathrm{RH} + \mathrm{CO} + \mathrm{M}. \text{ (decomposition.)}$$

In the region of pure continuous absorption below 2730A where the quantum yield of decomposition approaches unity, increasing the pressure had almost no effect on the yield. In this region, where there was no fluorescence, as well as in the diffuse predissociation bands, a decomposition mechanism was suggested as had been proposed by Herzberg. It differed from that of Norrish in assuming the presence of free radicals.

[116] Schou, S. A., and Henri, V., *Z. Physik*, **49**, 774 (1928); Henri, V., *Trans. Faraday Soc.*, **25**, 765 (1929); Schou, S. A., *J. chim. phys.*, **26**, 1 (1929).
[117] Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, **55**, 1766 (1933).
[118] For the influence of acids and alkalies upon the absorption spectra of aqueous solutions altering the amount of an enolic form, see Schou, S. A., *Compt. rend.*, **184**, 1452 (1927) and Fromageot, C., *J. chim. phys.*, **24**, 623 (1927).
[119] Smith, J. H. C., *loc. cit.*

$$RHCO + h\nu \longrightarrow R + HCO$$
$$R + HCO \longrightarrow RH + CO$$
$$R + R + M \longrightarrow R_2 + M$$
$$HCO + HCO \longrightarrow H_2 + 2CO$$
$$R + HCO + M \longrightarrow RHCO + M.$$

That some polymerization (yield 0.1) could still be observed at these wave-lengths suggested the possibility that the free radicals could induce polymerization in other molecules through the formation of intermediate compounds.

Particularly interesting results were obtained with the wave-length 3342A which lies between two band maxima, so that the absorption is ascribed principally to the weak underlying continuum. The result was a high quantum yield for decomposition as in the short wave-length regions (0.72-0.82) and little or no polymerization. This observation and the gradual changes in the quantum yields of the two processes, with no sharp breaks, agreed with the gradual transition observed between the different absorption regions. The maximum probability of excitation to the upper electronic state which leads to dissociation occurs at about 3100A, very close to the point at which all rotational structure disappears from the bands.

The chief support advanced for the proposed dissociation mechanism was the subsequent [120] finding of hydrogen in the decomposition products by a new method of microanalysis,[121] although Leighton and Blacet had been unable to detect it in their original work. From the ratios of hydrogen to carbon monoxide found at three wave-lengths, (0.05 at 3130A, 0.10 at 2804A and 0.155 at 2537A), it was concluded that the fraction of the molecules yielding hydrogen increases linearly from 10 per cent at 3130 to 31 per cent at 2537A. These observations made at 300 mm. favored a short-chain reaction at room temperatures.

Leermakers [122] found that at temperatures above 80°C., and with irradiation of acetaldehyde by 3130A, the short-chain reactions leading to the production of hydrogen were replaced by or accompanied by longer chains leading to the production of methane along with carbon monoxide. The rate of the chain reaction was proportional to the concentration of the aldehyde and to the square root of the light intensity. Below temperatures of 160°C., a term, 0.3 I, had to be added to the rate equation to cover that photolysis which was not a part of the chain reaction. The quantum yield increased enormously with the temperature reaching 310 at 309.5°C., when light of low intensity was used. In the case of formaldehyde, Leermakers also found a chain length of 100 at temperatures between 100° and 400°C. On the other hand, the acetone decomposition is not similarly affected, the quantum yield remaining at 0.76 at high temperatures. He suggests that acetone may follow the Norrish type of primary process, although acetaldehyde exhibits a chain mechanism involving methyl radicals. The energy of activation for the reaction: $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$ is 9.8 kcal. and that of the formaldehyde reaction $H + HCHO \rightarrow H_2 + HCO$ is 16.2 kcal. Patat [123] uses the para-hydrogen conversion method for calculating the free radical concentrations. Blacet and Volman now believe the Leermakers chain mechanism for the reaction at high temperature applies also at room temperatures.

[120] Blacet, F. E., and Roof, J. G., *J. Am. Chem. Soc.*, **58**, 278 (1936); Blacet, F. E., and Volman, D., *Ibid.*, **60**, 1243 (1938).

[121] Blacet, F. E., and MacDonald, G. D., *Ind. Eng. Chem., Anal. Ed.*, **6**, 334 (1934). Compare Franke, A., and Pollitzer, E., *Monatsh.*, **34**, 797 (1913).

[122] Leermakers, J. A., *J. Am. Chem. Soc.*, **56**, 1537 (1934).

[123] Patat, F., *Naturwiss.*, **24**, 62 (1936); *Z. physik. Chem.*, **32B**, 274 (1936).

Pearson [124] failed to detect free radicals in the primary products of the photolysis of acetaldehyde and of propionaldehyde (as well as methylbutyl ketone) by their action on metallic mirrors, although they could be detected in the case of acetone, methyl ethyl ketone and diethyl ketone. Later, however, Pearson and Purcell [125] succeeded in demonstrating the presence of free radicals in the case of acetaldehyde and attributed previous failures to the presence of a thin film of polymerized aldehyde upon the mirrors. Since, when equal quantities of acetaldehyde and acetone were irradiated, six times as many free radicals were found as when the aldehyde alone was used, it was suggested that there may be some underlying difference in the mechanisms of the photolyses of aldehydes and ketones, although it was concluded that free radicals must be admitted, as Leighton and Blacet maintained, to play some part in the photolysis of aldehydes. Glazebrook and Pearson,[126] who have measured the relative quantities of free radicals formed by the dissociation of a number of ketones, state that in the case of acetone, the acetyl and methyl radicals are formed in comparable quantities. The former, however, rapidly combine with one another to form diacetyl, and have a short life, possibly dissociating further into a methyl radical and carbon monoxide.

It was earlier claimed by Ghosh and Nandy [127] that the decomposition in dilute aqueous solutions involves a chain reaction, since the quantum yield is 13.4. They found the reaction to be unimolecular, the velocity coefficient being independent of the initial concentration. There was a small but definite temperature coefficient.

Discherl [128] states that acetoin, $CH_3CH(OH)COCH_3$, is formed when aqueous solutions of acetaldehyde or of pyruvic acid are irradiated by ultraviolet light, but the mechanism is not clear. A quartz apparatus designed for carrying out this reaction has been described by Benson and Cadenhead.[129]

The action of ultraviolet light on trimethylacetaldehyde was shown by Hinterberger [130] to cause the evolution of carbon monoxide. Conant, Webb and Mendum isolated isobutane from a sample of this compound allowed to decompose for many weeks in daylight in the absence of oxygen. By filter experiments, it was shown that light in the range 2950 to 3200A was effective. The addition of a small amount of hydroquinone decreased the decomposition to a third. Similar results were also obtained with dimethylacetaldehyde. Ultraviolet light also accelerated autoxidation of the trisubstituted aldehyde.

In the case of propionaldehyde, Leighton and Blacet [131] reported results very similar to those for acetaldehyde. They indicated their belief that there may be two distinct primary processes, one of which occurring to the extent of 80 per cent or more yields directly RH and CO, as postulated by Norrish. The other yields R_2, hydrogen (which could be detected), and carbon monoxide. They also extended their work to include *n*- and *iso*-butyraldehyde.[132]

The quantum yields in the case of acetaldehyde and propionaldehyde are

[124] Pearson, T. G., *J. Chem. Soc.*, 1718 (1934).

[125] Pearson, T. G., and Purcell, R. H., *J. Chem. Soc.*, 1151 (1935); 253 (1936); Glazebrook, H. H., and Pearson, T. G., *Ibid.*, 1777.

[126] Glazebrook, H. H., and Pearson, T. G., *J. Chem. Soc.*, 567 (1937).

[127] Ghosh, J. C., and Nandy, S. K., *J. Indian Chem. Soc.*, **6**, 911 (1929); *Brit. Chem. Abs.*, **1930A**, 555.

[128] Discherl, W., *Z. physiol. Chem.*, **188**, 225 (1930).

[129] Benson, G., and Cadenhead, A., *J. Soc. Chem. Ind.*, **54**, 40 (1934).

[130] Hinterberger, H., Dissertation, Vienna, 1923; cited by Conant, J. B., Webb, C. N., and Mendum, W. C., *J. Am. Chem. Soc.*, **51**, 1248 (1929).

[131] Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, **54**, 3165 (1932).

[132] Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, **54**, 3165 (1932); **55**, 1766 (1933).

greatly reduced in the presence of small amounts of nitric oxide.[133] The photochemical decomposition of isovaleraldehyde involves two types of reactions, according to Norrish and Bamford.[134] One, in line with the usual Norrish mechanism, yields directly CO and isobutane and occurs to the extent of 47 per cent. The other, a new type of dissociation, gives rise to propylene and acetaldehyde, which then suffer further decomposition. In this case there is a rupture between the α and β carbon atoms of the hydrocarbon chain, producing an olefin and a simpler aldehyde. This type of reaction has been found to occur more readily in ketones than in aldehydes and is said to be facilitated by extending the length of the hydrocarbon chain.[135]

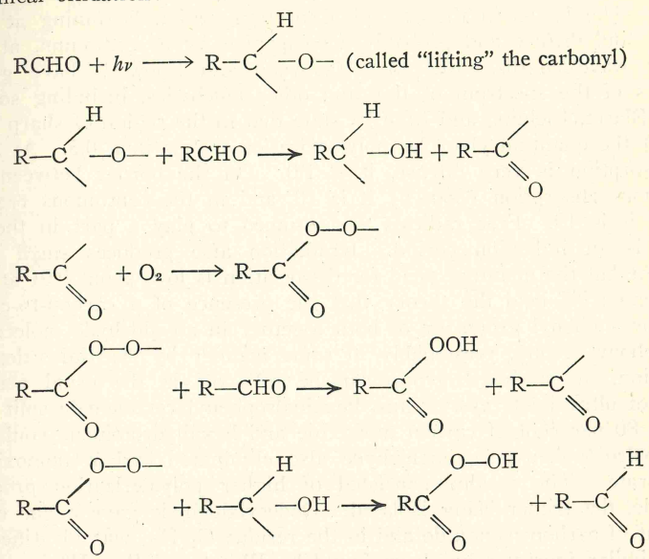
Oxidation of Aldehydes. It has been claimed that per-acids may be obtained by treating aldehydes with oxygen, under the influence of chemically active rays.[136] Taylor and Gould[137] found the photoöxidation of aqueous formaldehyde solutions to be a chain reaction. According to Carruthers and Norrish,[138] the process is

$$HCHO + 1/2O_2 \longrightarrow HCOOH.$$

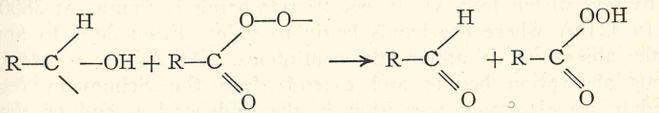
Part of the formic acid decomposes to water and carbon monoxide and part to hydrogen and carbon dioxide. 45 per cent of the formaldehyde yields formic acid, 20 per cent water and carbon monoxide, 3 per cent carbon dioxide and hydrogen, 32 per cent is polymerized and a slight amount is photolyzed. The latter process may be reduced by the presence of a trace of iodine vapor.

Acetaldehyde yields 59 per cent oxygen, 25 per cent carbon monoxide, 1.5 per cent ethylene, 4 per cent methane and a trace of hydrogen. The condensed products give the reactions of peroxides, and the compound $CH_3CO.O.O.COCH_3$ may be an intermediate product. The quantum efficiency of the process in the wave-length region 2480 to 2750A is 11 moles decomposed per quantum absorbed. (It is ten in the case of formaldehyde.) In the presence of nitrogen, the quantum efficiency for the formation of biacetyl is approximately 22. The formation of an intermediate peracetic acid had been postulated by Bowen and Tietz[139] who regarded it as the first step of a chain reaction. Its reaction with a molecule of acetaldehyde gives acetic acid, the formation of which had been noted by Bertholet and Gaudechon. On the other hand, its reaction with a second molecule of peracetic acid gives the comparatively stable intermediate peroxide the formula of which was given above. The rate of the reaction is, according to Bowen and Tietz, independent of the oxygen concentration and proportional to the acetaldehyde concentration and to the square root of the light intensity. It is essentially the same at various wave-lengths within the absorption band of the aldehyde. In hexane solutions, alcohol acts as an inhibitor and the reaction becomes directly proportional to the light intensity.

Further evidence for the chain nature of the oxidation of aldehydes both in light and darkness has been given by Bäckström,[140] who investigated particularly benzaldehyde and enanthaldehyde. The maximum yields amounted to about 10,000 for the former and 15,000 for the latter. He has also shown that the ketone-sensitized oxidation[141] of aldehydes has the same chain mechanism as the photochemical oxidation:



The chains are broken by the mechanism:



This mechanism was believed to be in agreement with the rates found by Bowen and Tietz in the case of gaseous acetaldehyde.

Bogert and McDonough[142] have studied the rates of autoxidation of seventeen aldehydes used in perfumery. With the exception of salicylaldehyde, they are subject to autoxidation in daylight and in darkness, the daylight rates being, except in the case of the cinnamaldehyde types, considerably greater than those in darkness. The temperature coefficients were the same for both the light and dark reactions.

Unsaturated Aldehydes. Acrolein is unaffected by diffused daylight in two months when exposed in sealed tubes, but sunlight solidifies about one-third of it in quartz tubes in twelve days and the mercury arc completely solidifies it in 1½ hours.[143]

Thompson and Linnett[144] have found its absorption spectrum to consist of two

[133] Mitchell, J. W., and Hinshelwood, C. N., *Proc. Roy. Soc.*, **159A**, 32 (1937).

[134] Norrish, R. G. W., and Bamford, C. H., *J. Chem. Soc.*, 1504 (1935).

[135] For the behavior of normal and isobutyraldehydes which, in the main, resemble acetaldehyde, see Leighton, P. A., Levanas, L. D., Blacet, F. E., and Rowe, R. D., *J. Am. Chem. Soc.*, **59**, 1843 (1937).

[136] Consortium für Elektrochemische Industrie, British Patent 16,849, July 22, 1913.

[137] Taylor, H. S., and Gould, A. J., *J. Phys. Chem.*, **37**, 367 (1933).

[138] Carruthers, J. E., and Norrish, R. G. W., *J. Chem. Soc.*, 1036 (1936).

[139] Bowen, E. J., and Tietz, E. L., *J. Chem. Soc.*, 23 (1930); see also Cantieni, R., *Z. wiss. Phot.*, **36**, 119 (1937) for the formation of a peroxide during the irradiation of paracetaldehyde in oxygen.

[140] Bäckström, H., *J. Am. Chem. Soc.*, **49**, 1460 (1927).

[141] Bäckström, H., *Z. physik. Chem.*, **B25**, 99 (1934).

[142] Bogert, M. T., and McDonough, E. G., *Drug and Cosmetic Ind.*, **32**, 312, 332, 514, 533, 536, 538, 540 (1933); *Chem. Abs.*, **27**, 4625 (1933).

[143] Moureu, C., Murat, M., and Tampier, L., *Ann. chim.*, **15**, 221 (1921); *Compt. rend.*, **171**, 1267 (1921); *Chem. Abs.*, **15**, 2220 (1921); **16**, 55 (1922); Moureu, C., Dufraisse, C., and Badoche, M., *Bull. soc. chim.*, **35**, 1572, 1591 (1924) have also investigated its oxidation in light.

[144] Thompson, H. W., and Linnett, J. W., *Nature*, **134**, 937 (1934); *J. Chem. Soc.*, 1452 (1935).

widely separated regions. Between 3800 and 2900A there are bands with fine rotational structure, at least at the long-wave end, and no underlying continuum. No fluorescence, however, could be observed on irradiation within this region, but polymerization occurred. The maximum absorption was found at 3450A. The bands in the second absorption region beginning at 2350A were narrow and diffuse and probably accompanied by a continuum, at least at the shorter wave-lengths. Recently, Eastwood and Snow[145] have given detailed analyses of the spectrum of this and other aldehydes, including some saturated ones. Blacet, Fielding and Roof[146] state that in the region of sharp bands (3660-3130A) the quantum yield for polymerization is less than 0.5. At 3020A where the absorption is very diffuse, it is 1.0. On the border between banded and continuous absorption (2804A) it is 10, and in the continuous region at 2654-2537A, it is 19. Free radicals are assumed to play a part in the mechanism. There is an induction period. Irradiation also produces small quantities of acetylene but the quantum yield for dissociation is low, about 0.01 at 3665A.

Sigmund[147] held the theory that the presence of a carbon-to-carbon double bond, or a phenyl group, or of both together in an aldehyde molecule, stabilizes the carbonyl group, presumably in some manner by "partial valences." After saturation, the carbonyl group can be split off in the usual manner by the action of ultraviolet rays. Thus, hexahydrophenylacetaldehyde split off gas containing 80 per cent of carbon monoxide and hexahydrotoluene could be isolated. Hexahydro-β-phenylpropionaldehyde also eliminated carbon monoxide but at a lower rate. The residue consisted of higher polymerization products of the aldehyde, the trimer being isolated. Dodecylaldehyde gave a gas containing 80 per cent of carbon monoxide and in the residue $C_{11}H_{24}$ was identified.[148]

A similar inertness has been found by Blacet and Roof[149] in crotonaldehyde which has an absorption spectrum resembling that of acetaldehyde shifted toward the red by several hundred A. It has discrete bands beginning at 3800A and continuing to 3245A where the bands begin to fade. From 3090 to approximately 2600A the absorption is apparently continuous. At 2550A a second region of continuous absorption begins and extends into the Schumann region. It is attributed to an electronic transition in the hydrocarbon end of the molecules. At 3660A only one quantum out of 150 was effective in causing a reaction, probably a polymerization. The wave-lengths 3130, 3020, 2804, 2654, 2537 and 2399A, all but the first of which are in regions of apparently continuous absorption, caused no detectable decomposition. Similar results were obtained when the aldehyde was subjected to the action of excited mercury atoms, but in the presence of oxygen a photochemical oxidation of the aldehyde vapors occurred.

Two explanations of this inertness in a region indicative of dissociation were suggested. The first, which relates the stability in some manner to the presence of conjugated double bonds, assumed that the absorption might be only apparently continuous, the energy of excitation being rapidly dissipated in other modes of vibration than that of the carbonyl group responsible for the absorption. More acceptable, however, would be the view that the continuous region implies, as usual, a true dissociation, but that this is followed by a rapid recombination. The need for the occurrence of three-body collisions may decrease in the case of such

[145] Eastwood, E., and Snow, C. P., *Proc. Roy. Soc.*, **149A,** 434, 446 (1935).

[146] Blacet, F. E., Fielding, G. H., and Roof, J. G., *J. Am. Chem. Soc.*, **59,** 2375 (1937).

[147] Sigmund, F., *Monatsh.*, **52,** 185 (1929).

[148] Müller, A., *Seifensieder-Ztg.*, **63,** 441 (1936); *Chem. Abs.*, **30,** 7556 (1936), notes a polymerization of phenylacetaldehyde in sunlight.

[149] Blacet, F. E., and Roof, J. G., *J. Am. Chem. Soc.*, **58,** 73, 608 (1936).

a complex molecule, the excess energy going into some kind of excitation. This was believed to be in line with the fact that the quantum yields for decomposition of the higher saturated aldehydes are less than unity in the continuous absorption region, decreasing with increase in the molecular weight.

To summarize the reactions of the aldehydes,[150] it may be stated that some on activation dissociate to yield carbon monoxide and hydrocarbons, although a certain percentage of the molecules appear to dissociate to give free radicals.[151] Furthermore, in the gas phase, the simpler aldehydes and ketones produce carbon monoxide and hydrocarbons, but the more complicated members tend to dissociate to yield simpler aldehydes or ketones and unsaturated hydrocarbons. Unsaturated aldehydes such as acrolein or crotonaldehyde are relatively inert.[152] Recently, a number of aldehydes have been studied in aqueous solution by Farkas and Hirschberg.[153] The quantum yields for molecules destroyed are: formaldehyde, 0.5; acetaldehyde, 2.5; propionaldehyde, 1.8; crotonaldehyde, much less than one. In the case of acetaldehyde, acetaldol is formed; the formation of an aldehyde molecule with free valences may be the primary process.

Ketones. Berthelot and Gaudechon[154] found acetone to be rapidly decomposed by ultraviolet light, the gas formed having 49 per cent carbon monoxide, 46 per cent ethane and but 5 per cent methane. In aqueous solutions, carbon dioxide was also formed. With sunlight and air, acetic acid was also formed.[155]

Henri and Wurmser[156] definitely showed the reaction to be related to the ultraviolet absorption spectrum of the carbonyl group.[157]

At first it was believed[158] that absorption in the region about the maximum was continuous, Noyes[159] stating that no fine structure or discontinuities had been reported in the absorption curve even when long path-lengths of acetone vapor at low pressures were studied. He believed it an open question as to whether it is justifiable to assume that this implies a primary dissociation process in analogy with the continuous spectra of diatomic gases, since in such complex molecules reasonance effects might lead to an overlapping of energy levels sufficient to preclude the appearance of any very marked banded structure. Noyes preferred to regard the primary process as of the type of predissociation by collision. More recently, however, Bowen and Thompson[160] using long

[150] Rollefson, G. K., *J. Phys. Chem.*, **41,** 259 (1937).

[151] See, however, Norrish, R. G. W., and Bamford, C. H., *Nature,* **140,** 195 (1937). They also investigate the reactions in liquid paraffin solution at 100°, the products consisting of CO, RH and R'H, the latter being produced by dehydrogenation of the solvent by the alkyl radicals.

[152] It has been observed by Kuhn, R., Badstübner, W., and Grundmann, C., [*Ber.*, **69B,** 98 (1936)] that pure crotonaldehyde does not undergo condensation with piperidine unless it has been exposed to sunlight or to a quartz lamp. The irradiation is believed to produce a compound, probably $CH_3CH=CHCOOH$, by autoxidation. This is thought to be necessary for the condensation.

[153] Farkas, L., and Hirschberg, Y., *J. Am. Chem. Soc.*, **59,** 2453 (1937).

[154] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151,** 478 (1910).

[155] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150,** 1164 (1910).

[156] Henri, V., and Wurmser, R., *Compt. rend.*, **155,** 503 (1912); see also Porter, C. W., and Iddings, C., *J. Am. Chem. Soc.*, **48,** 40 (1926) and Wiesler, K., *Z. angew. Chem.*, **40,** 1023 (1927).

[157] Bowen, E. J., and Thompson, H. W., *Nature,* **133,** 571 (1934); Norrish, R. G. W., *Nature,* **133,** 837 (1934); Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem. Soc.*, 1456 (**1934**); Scheibe, G., Povenz, F., and Lindström, C. F., *Z. physik. Chem.*, **B20,** 283 (1933). The influence of various substituents has been studied by Lowry, T. M., and Lishmund, R. E., [*J. Chem. Soc.*, 1313 (**1935**)] and by Herold, W., [*Z. physik. Chem.*, **B18,** 265 (1932); *Z. Elektrochem.*, **38,** 633 (1932)]. The effects of solvents of varying polarity have been described by Wolf, K. L., [*Z. physik. Chem.*, **2B,** 39 (1929)], Kremann, R., Pestemer, M., and Bernstein, P., [*Monatsh.*, **61,** 351 (1932)], and Pestemer, M., [*Z. Elektrochem.*, **40,** 493 (1934)].

[158] Ley, H., and Arends, B., *Z. physik. Chem.*, **12B,** 132 (1931); Scheibe, G., and Lindström, C. F., *Z. physik. Chem.*, **B12,** 387 (1931).

[159] Noyes, W. A., Jr., *Rev. Modern Physics,* **5,** 285 (1933). Noyes has recently attempted an interpretation of the near ultraviolet absorption spectrum, *Trans. Faraday Soc.*, **33,** 1495 (1937).

[160] Bowen, E. J., and Thompson, H. W., *Nature,* **133,** 571 (1934).

columns of acetone vapor at pressures of 0.5 to a few millimeters detected four groups of bands each composed of about 25 diffuse bands. Their centers were at 3150, 2900, 2710, and 2570A. At higher pressures (up to about 200 mm.) the bands widened to produce a region of continuous absorption extending from 3200 to 2400A, with its maximum at 2800A, characteristic of compounds containing the carbonyl group. They discarded the hypothesis that predissociation splits a carbon-hydrogen or carbon-carbon bond, and attributed the diffuseness of the bands merely to an unresolved close packing of rotation lines, which they believed similar to that in the spectra of other Y-shaped molecules.

Further evidence came from a study of fluorescence. It was found by Damon and Daniels[161] that acetone vapor shows a green fluorescence when irradiated by wave-lengths shorter than 3130A. It is blue in the presence of a trace of oxygen, but changes to green when the latter has been removed by a photoöxidation of some of the acetone. Norrish, Crone and Saltmarsh,[162] found the absorption spectrum of acetone vapor to consist of a continuous band between about 3000 and 2200A with a few faint maxima, and a region of discrete absorption between 3340A and about 2950A, thus slightly overlapping the continuous region. Fluorescence was produced only by absorption in the continuous region, its maximum intensity being excited by the absorption of the wave-length 3050A. The fluorescence spectrum excited by the mercury arc consisted of three diffuse bands with maxima at 5100, 5600 and 6100A.[163] The specific effect of oxygen was attributed to the removal of oxygen by excited acetone and the formation of a second transient fluorescent substance. The fluorescence of acetone vapor was unaffected by the addition of nitrogen, but its intensity increased with increasing pressure of acetone vapor.[164] The characteristics of the fluorescence were thought to argue against the concept that it arises from excited molecules of the usual type formed in the continuous region. Furthermore, the assumption of Bowen and Thompson that the apparently continuous bands are really composed of unresolved closely packed rotation lines would not account for the abrupt appearance of fluorescence observed to occur at the wave-lengths at which the diffuseness of the bands begins.[164a]

Norrish suggested that the energy absorbed by the chromophoric carbonyl group passes to some other linking or linkings in the molecule by a process similar to the radiationless transfer in a collision of the second kind. A portion may lead to the formation of free radicals by decomposition, a portion may lead to a decomposition of the molecule by a process of the type discussed for aldehydes which produces carbon monoxide and ethane, and a portion, less than 3 per cent, may be lost by fluorescence.

Although Bowen and Watts,[164b] who used nonmonochromatic light, reported a quantum yield of 1.8 for the photolysis of acetone vapor, Damon and Daniels[165] found it much lower, only about one of every five or six absorbed quanta leading to chemical reaction, including both decomposition and condensation processes. The yields were about the same for radiations of 3130 and 2650A. Decreasing the

[161] Damon, G. H., and Daniels, F., *J. Am. Chem. Soc.*, **55**, 2363 (1933).

[162] Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem. Soc.*, 1456 (1934).

[163] The visible and diffuse fluorescence is accompanied also by ultraviolet emission of fine sharp lines, interpreted as predissociation in emission by Crone, H. G., and Norrish, R. G. W., *Nature*, **132**, 241 (1933). See also Padmanabhan, R., *Proc. Indian Acad. Sci.*, **5A**, 594 (1937); *Chem. Abs.*, **31**, 8379 (1937). Matheson, M. S., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **60**, 1857 (1938).

[164] But compare, Fisk, C. F., and Noyes, W. A., Jr., *J. Chem. Physics*, **2**, 654 (1934).

[164a] Norrish, R. G. W., *Nature*, **133**, 837 (1934).

[164b] Bowen, E. J., and Watts, H. G., *J. Chem. Soc.*, 1607 (1926).

[165] Damon, G. H., and Daniels, F., *J. Am. Chem. Soc.*, **55**, 2363 (1933).

intensity to about one-tenth increased the quantum yield by more than 50 per cent. Reducing the acetone pressure to one-tenth atmospheric reduced the quantum yield to roughly one quarter that at atmospheric pressure.

Condensation reactions occurred only in the presence of traces of moisture. It was suggested that under these conditions diacetone alcohol was produced. The latter could be photolyzed by the wave-length 3650A to the same products of photolysis as those of acetone. The alcohol shows a green fluorescence when irradiated by the wave-lengths 3650, 4050 or 4360A, but only slight fluorescence at 3130A or shorter wave-lengths.

Damon and Daniels found the products of photolysis of acetone to include carbon monoxide, ethane, methane, hydrogen and free carbon. Their mechanism was based on the assumption that activated molecules split off carbon monoxide, the remaining methyl groups combining in more than half the molecules to form ethane. Norrish, Crone and Saltmarsh found 46.6 per cent carbon monoxide, 44.2 per cent ethane and 9.2 per cent of methane and confirmed the quantum yield measurements of Damon and Daniels. Light absorbed both in the regions of discrete and continuous absorption leads to decomposition, the yields being 0.2 at 3150A and 0.4 at 2650A. The full mercury arc gives somewhat less than 10 per cent of methane, possibly derived from a photoreaction in some liquid acetone also present. They believed the primary process to consist, as discussed in connection with their fluorescence observations, in the formation of free methyl radicals and the liberation of carbon monoxide. That the quantum yields were low, even in the continuous region, was accounted for only to a slight extent by the observed fluorescence. They preferred to conceive of the absorbed energy being for the most part degraded to heat by a process of internal stabilization in which the energy absorbed by the carbonyl group is divided up among the various forms of motion possible in the complex molecule. The theory of Norrish is of considerable importance in emphasinzing the possibility that energy absorbed in producing an electronic transition in one part of a molecule need not remain localized if the molecule is complex. The energy absorbed by the carbonyl group amounts to about 90 kcal. It is then partly transferred by resonance to the part of the molecule to be decomposed, about 25-65 kcal. being required for each linking to be broken. The formation of carbon monoxide suggested the simultaneous breaking of two linkages.[166]

Spence and Wild[167] believe that at temperatures below 60°, the primary process may consist in the rupture of but one linking with the formation of methyl and the acetyl radicals, since they were able to isolate large volumes of biacetyl from the liquid products of the photolysis of acetone. They found the ratio of the volume of ethane produced to that of carbon monoxide to be 1.5. At higher temperatures, however, the ratio is unity, and some methane is formed,[168] suggesting that under these conditions, the acetyl radical is short-lived. In the banded absorption region, the decomposition is slow and the ethane to carbon monoxide ratio is nearly one.

The reaction is increased by an increase of temperature, Winkler[169] finding

[166] Norrish, R. G. W., *Acta Physicochim. U.R.S.S.*, **3**, 171 (1935); *Chem. Abs.*, **30**, 2493 (1936).

[167] Spence, R., and Wild, W., *Nature*, **138**, 206 (1936); *J. Chem. Soc.*, 352 (1937).

[168] See also Taylor, H. S., and Rosenblum, C., [*J. Chem. Phys.*, **6**, 119 (1938)], who investigated the reaction in the presence of hydrogen. They believe the major primary process to be dissociation to methyl radicals, and consider especially the activation energies of the secondary processes, concluding the ethane to result either from a wall reaction with zero activation energy or from a bimolecular process of small activation energy.

[169] Winkler, C. A., *Trans. Faraday Soc.*, **31**, 761 (1935).

the quantum yield at 100°C. to be five times that at 60°C. This higher yield is maintained up to 400°C. The effect of temperature is much greater when the irradiation is by longer wave-lengths than by shorter ones. This may be due to the fact that the thermal energy of the molecule contributes more to the dissociation process when small quanta are absorbed than when larger ones are employed. At 400°C., the reaction products included a considerable quantity of methane and unsaturated compounds, indicative of the photochemical formation of ketene, $CH_2=C=O$. Leermakers [170] also found the quantum yield for carbon monoxide formation to be nearly unity in the temperature range 200° to 400°C., the carbon monoxide in the reaction products decreasing from 50 per cent to approximately 33 per cent. He also found that methyl radicals do not initiate a chain decomposition of acetone below 400°C.

Mention has not yet been made of the fact that the absorption by acetone increases from a minimum at about 2115A toward shorter wave-lengths, photolysis being pronounced below 2000A.[171] A vibrational analysis of the group of bands extending from 1960 to about 1800A has been given by Noyes, Dunning and Manning,[172] who photographed the spectrum down to 1200A and found other bands ascribed to different electron transitions below 1800A. According to Manning,[173] wave-lengths in the range 1900-2000A have little effect on acetone at pressures around 100 mm. The most effective ones are those shorter than 1700A; these produce increased amounts of hydrogen. At very low pressures (0.025 mm.), however, wave-lengths in the range 1850 to 2000A are more effective, but form only small amounts of gaseous hydrocarbons. The presence of a condensed nonvolatile hydrocarbon was suspected. Howe and Noyes [174] find that in this range the quantum yield is independent of the intensity, but increases with decreasing acetone pressure to a limit of 0.65. It is increased by the addition of nitrogen, ethane or carbon dioxide.

In hexane solution, the rate of decomposition is less than when the acetone is in the vapor form, and the quantum yield decreases with increasing acetone concentration.[175] Gases are not evolved and the chief products are a substance capable of absorbing bromine readily, and an alcohol, probably dimethyl-*n*-hexyldimethylcarbinol. Similarly, the reaction in carbon tetrachloride as solvent evolves no gas. In benzene solution, no photochemical reaction occurs.

In an aqueous solution, the production of formaldehyde as well as of acetic acid has been noted by Qureshi and Taher.[176] The quantum yields varied between 0.13 and 0.14 for concentrations 0.05 to 0.5 molar in acetone. The temperature coefficient of the rate was 1.52.[177]

Berthelot and Gaudechon [178] observed that one cc. of a 10-per cent solution of dihydroxyacetone evolved 0.2 cc. of almost pure carbon monoxide during 12 hours of exposure to sunlight. They also studied the behavior of diethylketone.[179]

[170] Leermakers, J. A., *J. Am. Chem. Soc.*, **56**, 1899 (1934).

[171] Ley, H., and Arends, B., *Z. physik. Chem.*, **12B**, 132 (1931).

[172] Noyes, W. A., Jr., Dunning, A. B. F., and Manning, W. M., *J. Chem. Physics*, **2**, 717 (1934); **3**, 131 (1935); Howe, J. P., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **58**, 1404 (1936).

[173] Manning, W. M., *J. Am. Chem. Soc.*, **56**, 2589 (1934).

[174] Howe, J. P., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **58**, 1404 (1936).

[175] Bowen, E. J., and de la Praudière, E., *J. Chem. Soc.*, 1503 (**1934**); Bowen, E. J., and Horton, A. T., *J. Chem. Soc.*, 1685 (**1936**).

[176] Qureshi, M., and Taher, N. A., *Nature*, **127**, 522 (1931); *J. Phys. Chem.*, **36**, 2670 (1932).

[177] For the photoöxidation of acetone vapor, see P. Fugassi, *J. Am. Chem. Soc.*, **59**, 2092 (1937).

[178] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 401 (1912).

[179] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151**, 478 (1910).

Norrish and Appleyard [180] found that, in the light of a mercury arc, about 80 per cent of the molecules of methylethylketone which decompose yield carbon monoxide and a mixture of ethane, propane and butane, the remainder forming ethylene and acetaldehyde.[181] Methylbutylketone yielded propene and acetone. In the range 2480 to 2770A the quantum yield of the decomposition of this ketone at 760 mm. and 127°C. by the process yielding carbon monoxide, methyl and butyl radicals is approximately 0.03, and by that yielding acetone and methylethylene, 0.27. That for condensation or polymerization is approximately 0.04.[182]

The absorption spectrum is diffuse and fluorescence is not observed. Similarly, dipropylketone exhibits two types of change on irradiation.[183] One type (37 per cent of the molecules decomposed) yields carbon monoxide and hexane, and the other (63 per cent) forms ethylene and methylpropylketone. In this reaction, Pearson and Purcell [184] detected the formation of the propyl radical by the mirror test and gave its half-life period as 2.3×10^{-3} second. In cyclohexanone, 10-per cent solutions of methylbutyl ketone and dipropylketone yield 98 per cent of methylethylene and ethylene, respectively, at 20°C. But at 100°C., dipropylketone gave also carbon monoxide and ethane. Two mechanisms accordingly seem necessary. One involves activated molecules with relatively long lives which are readily destroyed by collisions with the solvent molecules. The other involves excited molecules of such short life that the solvent molecules have no time to intervene between the time of activation and the subsequent decomposition.[185]

Saltmarsh and Norrish [186] have decomposed the vapors of cyclopentanone, cyclohexanone and cycloheptanone in the light of a quartz mercury arc. From 80 to 95 per cent of the last-named ketone decomposed to give cyclohexane and carbon monoxide and 4 per cent went to methylethylene. Of the cyclohexanone, 92 per cent gave carbon monoxide and cyclopentane and 8 per cent went to ethylene, methylethylene and carbon monoxide. Half of the cyclopentanone gave ethylene and carbon monoxide and half went to a mixture of propylethylene, *sym*-dimethylethylene and carbon monoxide.

Irradiation of isopropenylmethyl ketone by means of a quartz lamp produces in five days a solid polymer, soluble in acetone and precipitated as a colorless powder by methyl alcohol.[187] Under the same conditions, neither propenylmethylketone nor mesityl oxide polymerizes. The polymerization could take place by 1,4-addition as with rubber, through the carbonyl group analogous to the polyoxymethylenes and by the ethylene linkage with the formation of a paraffin derivative. Combinations of these methods of polymerization would lead to three-dimensional structures, but the solubility of the product did not support the occurrence of such a complication. The molecular weight of the polymer, as determined by the Staudinger viscosity method, was 34000.

[180] Norrish, R. G. W., and Appleyard, M., *J. Chem. Soc.*, 874 (**1934**). For results at 100° in liquid paraffin solution, see Norrish, R. G. W., and Bamford, C. H., *Nature*, **140**, 195 (1937); Norrish, R. G. W., *Trans. Faraday Soc.*, **33**, 1521 (1937). Here the free radicals react mainly with the solvent rather than combine together.

[181] At 3130A, 11 per cent of the reaction goes to diketones. Biacetyl is also formed when the irradiation is in the range 1850 to 2000A. In this range the quantum yield for carbon monoxide formation increases from 0.7 to 0.88 as the pressure decreases from 90 mm. to 0.1 mm. The total quantum yield for the decomposition approaches unity at low pressures. Ellis, V. K., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **60**, 2031 (1938).

[182] Bloch, B. M., and Norrish, R. G. W., *J. Chem. Soc.*, 1638 (**1935**).

[183] Bamford, C. H., and Norrish, R. G. W., *J. Chem. Soc.*, 1504 (**1935**).

[184] Pearson, T. G., and Purcell, R. H., *J. Chem. Soc.*, 253 (**1936**).

[185] Norrish, R. G. W., and Bamford, C. H., *Nature*, **138**, 1016 (1936).

[186] Saltmarsh, O. D., and Norrish, R. G. W., *J. Chem. Soc.*, 455 (**1935**); see also Norrish, R. G. W., *Acta Physicochim. U.R.S.S.*, **3**, 171 (1935); *Chem. Abs.*, **30**, 2493 (1936).

[187] Staudinger, H., and Ritzenthaler, B., *Ber.*, **67B**, 1773 (1934).

According to Bowen and de la Praudière,[188] liquid benzophenone at 100°C., showed no change after irradiation for nine hours with a mercury arc, and acetophenone no change after seven hours. When a 0.1 molar solution of benzophenone in hexane was irradiated, benzopinacol crystallized out, being formed with a quantum efficiency of 0.04. None was formed when carbon tetrachloride was the solvent.

The quantum efficiency of the photopolymerization of biacetyl in solutions in hexane or ether by wave-lengths between 4360 and 3660A is greater the more dilute the solutions. Bowen and Horton[189] account for this by an explanation which Bowen also used to account for the more rapid decomposition of various ketones in solution than in the pure liquid state. This was to the effect that the primary excited level is not reactive but passes, if not deactivated by a collision within 10^{-12} second, into a second excited level which is reactive.

Ketene. The absorption spectrum of ketene vapor consists of a series of regularly spaced diffuse bands in the region of carbonyl absorption, 3700 to 2600A. The maximum absorption is somewhat displaced to longer wave-lengths occurring at 3100A.[190] No difference exists between the absorption spectra of aldoketenes of the type $H_2C{=}CO$ and ketoketenes, $R_2C{=}CO$. There is also a region of continuous absorption beginning at 2200A and ascribed to the ethylene linking. Fluorescence is lacking in ketene.

Irradiation with the mercury arc leads to decomposition with the formation of two volumes of carbon monoxide and one of ethylene. Norrish, Crone and Saltmarsh believe that light energy absorbed by the carbonyl group is transferred to the ethylene group with consequent rupture.

$$CH_2{=}CO + h\nu \longrightarrow CH_2 + CO$$

This is followed by the process:

$$CH_2 + CH_2{=}CO \longrightarrow C_2H_4 + CO.$$

Ross and Kistiakowsky[191] interpreted the above-mentioned primary process as due to predissociation in accordance with the nature of the absorption spectrum, no collisions being necessary. They found the decomposition to occur with a quantum yield of approximately unity at 3130A. The accumulation of ethylene stops the reaction. A solid film deposited on the walls of the reaction vessel must have the composition $(CH_2)_n$ since no free carbon deposits were obtained and no hydrogen was liberated.

Ross and Kistiakowsky thought the additional energy required to break the double bond over that available in the absorbed quantum might be derived from the resonance energy of the carbon monoxide formed in the decomposition. The secondary reaction of Norrish was rejected because the quantum yield proved to be unity. The methylene radicals formed in the primary process must react with each other to form ethylene. The slowing down of the reaction by ethylene must be ascribed to the reaction of methylene groups with ethylene with formation of the solid polymer. Thus, methylene radicals appear to combine readily to ethylene in a bimolecular reaction, although methyl radicals do not combine so readily to form ethane. At 3660A, where the banded structure is more pronounced and

[188] Bowen, E. J., and de la Praudière, E., *J. Chem. Soc.*, 1503 (1934).

[189] Bowen, E. J., and Horton, A. T., *J. Chem. Soc.*, 1505 (1934).

[190] Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem. Soc.*, 1533 (1933); Lardy, G. C., *J. chim. phys.*, 21, 353 (1924)

[191] Ross, W. F., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, 56, 1112 (1934).

predissociation less probable, the quantum yield of the reaction, which occurs but slowly at this wave-length, appears to be less than unity.

Norrish, Crone and Saltmarsh[192] do not agree that the observed quantum yields necessarily exclude the occurrence of their secondary reaction, since it is known that in polyatomic molecules, as acetone, etc., the quantum yield of the primary process may be less than unity throughout a considerable portion of a region of continuous absorption.

Diketones. In α-dicarbonyl compounds, such as glyoxal, the conjugation of the double bonds moves the absorption into the visible.[193] Glyoxal vapor, which has its maximum absorption between 4550 and 4123A, gives as the main products of decomposition carbon monoxide and a solid consisting of a polymer of the hitherto unknown glycerosone, $CH_2OH{\cdot}CO{\cdot}CHO$. About 2 per cent of hydrogen was also obtained as a result of a second reaction.[194]

Schwenk and Borgwardt[195] prepare unsaturated α, β-diketones by subjecting aromatic, hydroaromatic or aliphatic compounds in which a methylene group is directly coupled to an ethylene linkage, to the action of selenium dioxide and ultraviolet rays without heating. Thus, from α-indene is produced a ketone, $C_{10}H_{14}O$.

Biacetyl vapor is decomposed by ultraviolet rays with the production of ethane and carbon monoxide. An aqueous solution yields acetic acid and acetaldehyde.[196] Observations by Grossmann[197] on the absorption spectrum of ethylacetoacetate show that it is decomposed by ultraviolet rays, yielding mainly ethyl acetate and acetic acid. Under the same conditions, acetylacetone gives acetic acid and acetone.[198] Vitoria[199] finds that light from a quartz lamp causes partial polymerization and decomposition of gaseous acetylacetone with formation of carbon monoxide. With light of wave-lengths longer than 3050A, only polymerization occurs. Liquid acetylacetone, or its solution in carbon tetrachloride, undergoes a decided polymerization, but does not decompose to yield carbon monoxide. Walker and Wild[200] find acetyl peroxide to yield on photochemical decomposition, carbon dioxide, methane and some ethane.

Carbohydrates. In contrast to the observations of Bielecki and Henri[201] and of Niederhoff,[202] Henri and Schou[203] found that solutions of very pure dextrose showed no indication of an absorption band due to the carbonyl group at 2800A, most of the molecules having a ring structure. Alkaline solutions, however, exhibit the band, the number of molecules in the aldehydic form depending on the age, temperature and pH of the solution. Similar conclusions have

[192] Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Am. Chem. Soc.*, 56, 1644 (1934).

[193] Lüthy, A., *Z. physik. Chem.*, 107, 302 (1923); Purvis, J. E., and McCleland, N. P., *J. Chem. Soc.*, 101, 1810 (1912); Neuberg, C., and Schou, S. A., *Biochem. Z.*, 191, 466 (1927); Marchlewski, L., Pizlo, J., and Urbanczyk, W., *Biochem. Z.*, 264, 437 (1933).

[194] Norrish, R. G. W., and Griffiths, J. G. A., *J. Chem. Soc.*, 2829 (1928).

[195] Schwenk, E., and Borgwardt, E., German P. 608,136, Jan. 17, 1935, to Schering-Kahlbaum, A.-G.; *Chem. Abs.*, 29, 6246 (1935).

[196] Porter, C. W., Ramsperger, H. C., and Steel, C., *J. Am. Chem. Soc.*, 45, 1827 (1923).

[197] Grossmann, P., *Z. physik. Chem.*, 109, 305 (1924); *Chem. Abs.*, 19, 39 (1925).

[198] Morton, R. A., and Rosney, W. C., *J. Chem. Soc.*, 706, 713 (1926) and Acly, H. E., and French, H. S., *J. Am. Chem. Soc.*, 49, 847 (1927) report absorption data on these and related compounds. The enolic and ketonic forms are distinguishable by bands near 2500 and 2700A, respectively.

[199] Vitoria, A. P., *IX Congr. intern. quim. pura applicata*, 2, 334 (1934); *Chem. Abs.*, 29, 7811 (1935).

[200] Walker, O. J., and Wild, G. L. E., *J. Chem. Soc.*, 1132 (1937).

[201] Bielecki, J., and Henri, V., *Ber.*, 46, 3627 (1914).

[202] Niederhoff, P., *Z. physiol. Chem.*, 165, 130 (1927); 167, 310 (1927); 174, 300 (1928).

[203] Henri, V., and Schou, S. A., *Z. physiol. Chem.*, 174, 295 (1928).

been reported for a number of other sugars, including galactose, levulose, *l*-arabinose, rhamnose, maltose and lactose.[204]

The variations in the absorption exhibited by these sugars under various conditions of pH and the effects of impurities may perhaps account for the diverse statements which have been made in regard to their susceptibilities to photolysis. It is generally agreed that aqueous solutions of dextrose, galactose and mannose are not affected by sunlight, although changes[205] may be produced in the presence of such sensitizers as iron or uranium salts.[206] Ghosh and Rakshit[207] claim that visible light increases somewhat the rate of oxygen absorption by glucose or fructose in the presence of cerium hydroxide as catalyst.

Irradiation of 0.1 to 50 per cent glucose solutions with a mercury-vapor arc for fifteen minutes to five hours causes, according to Dillman,[208] no apparent change in optical rotation nor in their ability to reduce alkaline copper tartrate solution. de Fazi[209] believed that sugar solutions which had been irradiated six hours fermented more rapidly than untreated solutions. The induced oxidation of glucose by glutathione is said to be markedly accelerated by light; photosensitizers further accentuate the reaction.[210]

The formation of acid in irradiated dextrose solutions was noted by Euler and Lindberg,[211] who showed that on further action of the ultraviolet rays, there resulted a gaseous mixture containing 15 per cent carbon dioxide, 40 per cent carbon monoxide and 40 per cent hydrogen. Berthelot and Gaudechon,[212] however, found approximately equal volumes of carbon monoxide and methane and about six times as much hydrogen. More recently, Bernoulli and Cantieni[213] noted that at the beginning of the reaction much more hydrogen than carbon monoxide is evolved, but that later the reverse is true. The decomposition was accelerated by acids and retarded by alkalies. No optically active decomposition products were formed, and the decrease in glucose as measured by rotation was not proportional to the amount of carbon monoxide evolved.

Ketoses were found by Berthelot and Gaudechon,[214] to undergo photolysis more readily, and to behave in a manner similar to that of acetone. Levulose, sorbose, perseulose, erythrulose and dihydroxyacetone each gave carbon monoxide, hydrogen and the alcohol with one carbon atom less than the parent sugar. Extreme ultraviolet rays caused secondary reactions, in which carbon dioxide and methane were

[204] Marchlewski, L., and Kwiencinski, L., *Bull. Acad. Polonaise,* 255, 1926A; 379, 1927A; 257, 263, 271, 1928A; 317, 1929A; *Bull. soc. chim.,* **43,** 725 (1928); *Z. physiol. Chem.,* **169,** 300 (1927); Marchlewski, L., and Gabryelski, W., *Bull. Acad. Polonaise,* 397, 1933A; Marchlewski, L., and Urbanczyk, W., *Ibid.,* 409, 1933A; *Biochem. Z.,* **261,** 393 (1933); Fischler, F., Hauss, H., and Täufel, K., *Biochem. Z.,* **265,** 181 (1933); Braun, E., *Ber.,* **63B,** 1972 (1930); Kwiencinski, L., Mayer, J., and Marchlewski, L., *Z. physik. Chem.,* **176,** 292 (1928); Bednarczyk, W., and Marchlewski, L., *Bull. Acad. Polonaise,* 140, 1937A; *Chem. Abs.,* **32,** 1576 (1938); Goos, F., Schlubach, H., and Schröter, G., *Z. physik. Chem.,* **186,** 148 (1930). For absorption data on glucosides, see Marchlewski, L., and Mayer, J., *Bull. Acad. Polonaise,* 111 (1929); Ramart-Lucas, Mme., and Rabate, J., *Compt. rend.,* **196,** 1493 (1933). For hexose phosphates, Neuberg, C., and Schou, S. A., Biochem. Z., **191,** 466 (1927).

[205] Berthelot, D., and Gaudechon, H., *Compt. rend.,* **155,** 831 (1912).

[206] Neuberg, C., *Biochem. Z.,* **39,** 158 (1912); Abelous, Aloy and Valdiguè, *Compt. rend. soc. biol.,* **96,** 1385 (1927).

[207] Ghosh, J. C., and Rakshit, P. C., *J. Indian Chem. Soc.,* **12,** 357 (1935); *Brit. Chem. Abs.,* **1935A,** 1329.

[208] Dillman, L. M., *J. Lab. Clin. Med.,* **17,** 236 (1931); *Chem. Abs.,* **26,** 3270 (1932).

[209] de Fazi, R., *Atti accad. Lincei,* **5,** 344, 901 (1927); *Chem. Abs.,* **21,** 4013 (1927); Sanzo, L., and Pirrone, F., *Atti accad. Lincei,* **13,** 613 (1931); *Chem. Abs.,* **26,** 2990 (1932).

[210] Palit, C. C., and Dhar, N. R., *J. Indian Chem. Soc.,* **11,** 661 (1934); *Brit. Chem. Abs.* **1934A,** 1314. See also *J. Phys. Chem.,* **32,** 1263 (1928).

[211] Euler, H., and Lindberg, E., *Biochem. Z.,* **39,** 410 (1912); *J. Chem. Soc.,* **102,** II, 407 (1912).

[212] Berthelot, D., and Gaudechon, H., *Compt. rend.,* **151,** 395 (1910).

[213] Bernoulli, A. L., and Cantieni, R., *Helv. Chim. Acta,* **15,** 119 (1932).

[214] Berthelot, D., and Gaudechon, H., *Compt. rend.,* **155,** 401, 1153 (1912); *Bull. soc. chim.,* **35,** 241 (1924); see also Beyersdorfer and Hess, *Ber.,* **57B,** 1708 (1924).

evolved and the solution became acid. Levulose gave about ten times as much carbon monoxide as of methane.[215] Maltose behaved similarly to dextrose and sucrose gave results intermediate between dextrose and levulose.

The decomposition of the latter sugar gave also formaldehyde and methanol.[216] It was believed that this sugar was very slowly decomposed by sunlight, 0.54 cc. of almost pure carbon monoxide being produced in two months.[217]

The use of this behavior of a 10 per cent fructose solution in ultraviolet actinometry, proposed by Berthelot and Gaudechon,[218] has been more recently studied by Bernoulli and Cantieni.[219] In dilute solutions (4.5 to 18 g. per liter), the velocity is proportional to the concentration but in strong ones (720 to 1080 g. per liter), it is constant. The proportion of carbon dioxide in the gases evolved varies inversely with the light intensity. Acids appear to be formed only in solutions heated to 80°C. The evolution of gases is accelerated by sodium chloride and retarded by potassium bromide and iodide and acids or bases. The photolysis also occurs in methanol or glycerol solutions and in these is more accelerated by small amounts of water than by larger ones. The reaction can be produced by radiations passing through glass, but is much slower than in quartz, since only those fructose molecules possessing the ketonic structure evolve carbon monoxide. Molecules with ring structures are believed to yield carbon dioxide. At ordinary temperatures, the reaction, once started, may continue for hours after stopping the irradiation, but at high temperatures, the after-effect is very slight. The course is believed to involve the intermediary formation of a peroxide, perfructose. A yellow color (photopyridine) developed by light in solutions of pyridine, water and fructose is more readily formed and more readily bleached than it is in solutions in which the fructose is replaced by glucose, galactose, sucrose or lactose. Acetone inhibits its formation. Methanol is almost without influence on the color reaction, but has a greater retarding influence on fading than has fructose. Pure ethanol retards color formation, but the color once formed is more stable in ethanol than in methanol.

Holtz[220] finds the ultraviolet irradiation of aqueous sugar solutions (glucose, fructose, arabinose) and sugar-like solutions (glycerol, sorbitol, glucosamine) to produce substances which form systems with strong negative redox potentials. The products are believed to accelerate the autoxidation of cysteine and adrenaline. Dubouloz[221] added eosin (1:5000) to a 0.05 molar solution of glucose in a phosphate buffer solution of pH 7.7, and freed the solution of dissolved oxygen. After sufficient illumination by a tungsten lamp, the oxidation-reduction potential descended to −210 mv., the equilibrium point of oxygen-free glucose solutions. Further illumination caused a further descent. If this did not exceed 350 mv., the phenomenon was reversible, and upon standing in the dark, the value −210 mv. was regained.

The oxidation of glucose by hydrogen peroxide in acid medium photosensitized by tungstic acid appears to follow the unimolecular rate law when the peroxide concentration is low and to be of zero order when it is high.[222] There is an

[215] Berthelot, D., and Gaudechon, H., *Compt. rend.,* **151,** 395 (1910).

[216] Bierry, H., Henri, V., and Ranc, A., *Compt. rend.,* **151,** 316 (1910); *Biochem. Z.,* **64,** 257 (1914); *Bull. soc. chim.,* **35,** 771 (1924).

[217] Berthelot, D., and Gaudechon, H., *Compt. rend.,* **155,** 401 (1912).

[218] Berthelot, D., and Gaudechon, H., *Compt. rend.,* **156,** 707 (1913).

[219] Bernoulli, A. L., and Cantieni, R., *Helv. Chim. Acta,* **15,** 119 (1932); Cantieni, R., *Ibid.,* **17,** 1528 (1934); **18,** 473, 933, 1420 (1935); **19,** 86, 94, 270, 276 (1936); *Ber.,* **69B,** 2286 (1936).

[220] Holtz, P., *Arch. exptl. Path. Pharmakol.,* **182,** 141 (1936); *Brit. Chem. Abs.,* **1936A,** 1094.

[221] Dubouloz, P., *Compt. rend. soc. biol.,* **116,** 435 (1934); *Chem. Abs.,* **28,** 6371 (1934).

[222] Banerjee, T., *J. Indian Chem. Soc.,* **14,** 59 (1937); *Chem. Abs.,* **31,** 5275 (1937). See also Ghosh, J. C., and Mukherjee, J., *Ibid.,* **6,** 231 (1929).

induction period, which increases with the peroxide concentration. The velocity varies as the square root of the intensity of absorbed light, but is independent of the glucose concentration. The quantum yield is somewhat greater than unity and the temperature coefficient, 1.1 to 1.2. Similar reactions occur with formaldehyde and fructose.

Neutral solutions of sucrose are hydrolyzed by ultraviolet light and become slightly acid.[223] The rate of hydrolysis increased with the duration of the exposure, probably because of the acid formation, although this may have been due to traces of a catalyst. According to Bierry, Henri and Ranc,[224] the ultraviolet hydrolysis is appreciable in 5 per cent sucrose solutions after twenty hours of irradiation at 40°C.; after 48 hours formaldehyde can be detected. A gas evolution begins after 72 hours and becomes marked on the fifth or sixth day of exposure. Of the combustible part of this gas, 50 per cent was carbon monoxide.

Berthelot and Gaudechon,[225] confirmed the presence of two stages in the hydrolysis of disaccharides by relatively long wave-lengths. The first stage does not evolve gas, but the second consists in the decomposition of the mixture of monoses produced in the first stage and so is accompanied by the evolution of gas. They disagreed with previous observers, in that they did not find that acid is formed during the process. Beyersdorfer and Hess [226] using carefully purified sucrose and conductivity water found that at 15-20°C. in $\frac{1}{8}$ molar solution, the effect of irradiation was hardly perceptible. At 70° and 100°C., the sugar was attacked energetically, the decomposition at first increasing slowly, then rapidly, with increasing temperature. After the addition of 0.3 to 0.6 gram of chlorophyll to 250 cc. of $\frac{1}{8}$ molar solution, irradiation for twelve hours at 100°C. produced no detectable change in the sucrose. Manganese chloride, potassium chloride, potassium bromide, and potassium iodide had little influence on the change, which, however, scarcely occurs in the presence of sodium acetate.

In 0.5 molar solution at 100°C., gas evolution begins in 15 minutes, and the acidity and reducing power increase about in proportion to the time. After about four hours, the solution becomes levorotatory and after 24 hours contains no further positively detectable amounts of optically active substances. The reducing power reaches its maximum after about 48 hours, then decreases proportionately with the time and more slowly than it had increased. A crystal of sucrose when exposed to ultraviolet rays at 70°C. becomes coated on the exposed surface with a brown layer of caramel.

Yajnik, Goyle and Wadhera [227] maintain that aqueous sucrose solutions contained in Jena glass vessels undergo inversion when exposed to tropical sunlight in the absence of acid, and that in the presence of 0.25 normal acid, the rate of inversion is increased by sunlight. Some have believed visible and near infrared rays to effect the inversion with a high quantum yield, the reaction having also a high temperature coefficient.[228] Tanret [229] finds sucrose to be hydrolyzed slowly and maltose and trehalose to be hydrolyzed less than 30 per cent as fast as sucrose

[223] v. Euler, H., and Ohlsen, H., *J. chim. phys.*, **9**, 416 (1911).
[224] Bierry, H., Henri, V., and Ranc, A., *Compt. rend.*, **152**, 1629 (1911).
[225] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 1016 (1912); **156**, 468 (1913).
[226] Beyersdorfer, P., and Hess, W., *Ber.*, **57B**, 1708 (1924); Taketomi, N., and Miura, K., *J. Soc. Chem. Ind. Japan*, **33**, 9B (1930).
[227] Yajnik, N. A., Goyle, D. N., and Wadhera, M. L., *Z. anorg. Chem.*, **225**, 24 (1935).
[228] Bhattacharya, A. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **6**, 879 (1929); *Brit. Chem. Abs.*, **A**, 555 (1930); *Z. anorg. Allgem. Chem.*, **199**, 1 (1931); see also Andant, A., and Rousseau, E., *Compt. rend.*, **186**, 365 (1928).
[229] Tanret, G., *Compt. rend.*, **202**, 881 (1936); *Bull. soc. chim. biol.*, **18**, 1344 (1936).
[230] Szalay, S., *Magyar Biol. Kutato Intezet Munkai*, **8**, 417 (1935-6); *Chem. Abs.*, **30**, 7041 (1936).

by ultraviolet rays. The effect on lactose was uncertain. Szalay [230] suggested that pure sucrose solutions were not affected, but that those containing traces of glucose as catalyst, showed increased reducing power and acidity, ascribed by him to the formation of glucuronic acid.

Souty [231] directed two pencils of light from the same source, differing only in the direction of their circular polarization, on two identical solutions of a sugar which exhibits mutarotation. Differences in the rate of mutarotation, giving temporary differences which reached more than 0.25° were observed, but the same final equilibrium was obtained. In monochromatic light, glucose gave a positive result at 5461A and a negative one at 5890-6A.

In the case of the trioses, raffinose, melesitose and gentianose, the first stage of the reaction did not appear to consist of the formation of a monose and a biose.[232] After the first stage of decomposition, the action was the same as in the case of the monoses.

When a concentrated aqueous solution of trihexosan is exposed to ultraviolet rays for 56 hours, 60 per cent conversion into hexahexosan occurs; further irradiation of the latter appears to have no action.[233] Irradiation of dextrinosan, $C_{12}H_{20}O_{10}$, affords hexahexosan.

Massol [234] stated that if solutions of soluble starch (prepared by heating for three hours at 150°C.) of 0.2 to 1 per cent concentration, are exposed at a distance of 10 centimeters, to the action of a mercury-vapor quartz lamp consuming 300 watts, the starch gradually loses the property of giving a blue color with iodine, the color undergoing an alteration similar to that observed when the iodine test is applied at various stages of starch conversion. The rate of transformation increases on decreasing the concentration and on acidifying the medium. As a result of the exposure also, the solution acquires reducing power (probably due to maltose) and becomes less precipitable by alcohol. The portion soluble in alcohol possesses reducing power and is dextrorotatory. The hydrolysis was not due to the acidity or temperature or to the small amount of hydrogen peroxide formed under the action of the rays. According to Bielecki and Wurmser,[235] the hydrolysis is accompanied by a partial oxidation, since there can be identified among the products, besides dextrins, reducing sugars, including pentoses, some formaldehyde and other similar substances.

Samec [236] found that on exposing thin layers of potato starch in presence of air to the rays of a quartz lamp, it became yellow and the odor of acraldehyde was observed. The properties of solutions obtained by heating starch so treated under pressure with water indicate that considerable peptization had occurred, together with a certain amount of oxidation and hydrolysis. The behavior on electrodialysis depends on the length of exposure to the ultraviolet, the amount of "gel" being smaller the longer the exposure. The phosphorus of the starch remains largely in organic combination. The cleavage products separated by ultrafiltration, although possessing a lower optical rotation, show the typical iodine colorations of the amylo-compound. Observations have also been made at 50°C. on starch which has been previously dried, or washed with hydrochloric acid and dried and exposed to ultraviolet light in a stream of dry nitrogen and in

[231] Souty, P., *Compt. rend.*, **199**, 198 (1934).
[232] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 1506 (1912).
[233] Pictet, A., and Vogel, H., *Rec. trav. chim.*, **48**, 843 (1929); *Brit. Chem. Abs.*, **1929A**, 1167.
[234] Massol, L., *Compt. rend.*, **152**, 902 (1911).
[235] Bielecki, J., and Wurmser, R., *Compt. rend.*, **154**, 1429 (1912).
[236] Samec, M., *Kolloid. Chem. Beih.*, **23**, 377 (1927); *Brit. Chem. Abs.*, **A**, 412 (1927).

closed vessels in an atmosphere of nitrogen, whereby oxidation and hydrolysis are prevented. The solutions prepared under pressure from the exposed starch are sometimes cloudy and deposit a precipitate on centrifuging. Wheat starch is also peptized by ultraviolet light, and in this case the behavior of the solution on electrodialysis is the reverse of that of the unexposed starch. As with potato starch, a relatively simple organic acid containing phosphorus is found in the anode cell on electrodialysis.

The changes which take place when starch, glycogen, inulin, dextrin, amylose and amylopectin are irradiated with the quartz mercury lamp have been followed quantitatively by Lieben, Löwe and Bauminger [237] in respect to lactic acid and reducing substance produced. The latter consists not merely of glucose but also of maltose and other reducing sugars, including traces of triose. Amylose and amylopectin are less affected than is starch.[238]

It is claimed by Tanret and Guillaume [239] that 2-per cent solutions of glucosides (salicin, amygdalin, etc.) and also certain esters may be hydrolyzed by exposures to wave-lengths in the range 1800 to 3100A for three to twenty-four hour periods. An increase in temperature or acidity of the medium increases the rate. In the case of nine glucosides, the order of hydrolysis differed when the hydrolyzing agent was ultraviolet rays, acids, and enzymes.[240] After twelve hours of irradiation, various glucosides were hydrolyzed to the following percents: helicin, 100 per cent, gentiopicrin, 59, coniferin, 55.4, amygdalin, 35.4, salicin, 31.1, picein, 23.3, arbutin, 13.4 and methylarbutin, 8.1 per cent. Floridoside (glyceryl α-galactoside) and α- and β-methylglucosides were hydrolyzed very slowly and xanthorhamnin not at all, although it absorbed the entire ultraviolet spectrum used. Acetylsalicylic acid, tropacocaine, homotropococaine, monobutyrin and asparagine were hydrolyzed more or less, but ethyl acetate, glycylglycine, *dl*-alanylglycine, glycyltyrosine, and urea were not.[241] Saponin is claimed by Wolf [242] to lose its toxicity after irradiation by ultraviolet in solution, so that it may be used as an emulsifying agent in food products without danger of producing hemolysis.

[237] Lieben, F., Löwe, L., and Bauminger, B., *Biochem. Z.*, **271**, 209 (1934).

[238] See also Isemura, T., *J. Chem. Soc. Japan*, **56**, 772 (1935); *Chem. Abs.*, **29**, 7352 (1935).

[239] Tanret, G., and Guillaume, A., *Compt. rend.*, **201**, 1057 (1935).

[240] Tanret, G., *Compt. rend.*, **202**, 881 (1936); *Bull. soc. chim. biol.*, **18**, 1344 (1936); *Brit. Chem. Abs.*, **1936A**, 572.

[241] Guillaume, A., and Tanret, G., *Compt. rend.*, **201**, 1057 (1935); *Bull. soc. chim. biol.*, **18**, 556 (1936); *Chem. Abs.*, **30**, 5503 (1936).

[242] Wolf, J., German Patent 524,892, June 3, 1927; *Chem. Abs.*, **25**, 4326 (1931).

Chapter 24

Acids and Other Aliphatic Compounds

The action of ultraviolet light on many organic acids or their salts leads to decomposition [1] of the latter, but in unsaturated acids the polymerizations and stereoisomeric transformations characteristic of the photochemical behavior of double bonds often occur.

Ley and Arends [2] showed that saturated mono- and di-carboxylic aliphatic acids, in vapor form, in hexane, or in aqueous solutions have an absorption band beginning at about 2400A, with a maximum at 2040-2070A. This maximum is ascribed to the carbonyl group, since it appears also in the chlorides and anhydrides of the acids. The nature of the absorption is not materially affected by ester formation, but is usually totally changed by salt formation. Sodium acetate, considered as typical of the salts of acetic acid, shows no maximum at 2040A, but continues to absorb the shorter wave-lengths with increasing intensity. The curve for formic acid lies somewhat nearer to the visible. Ramsperger and Porter [3] found the bimolecular form of formic acid primarily responsible for the absorption between 2260 and 2500A. Harris [4] believed the unimolecular form to agree in absorption with that of the other acids, having its maximum at 2050A.

Lederer [5] finds some specific absorption by all fatty acids between 2700 and 2800A, that of propionic extending to 2700A and stearic to 2800A. A confirmation has been given by Hartleb,[6] but the cause of this absorption has not yet been definitely established.

There is spectroscopic evidence for the formation of solvates of both esters and free acids in various solvents [7] and Herold [8] concludes from ultraviolet absorption measurements that the formation of solvates (hydrates or semiacetals) is a necessary preliminary to the dissociation of the fatty acids.

Acetic Acid

In the photolysis of acetic acid in the absence of air, Berthelot and Gaudechon [9] obtained a gas which contained 44 per cent of carbon dioxide, 17 per cent of carbon monoxide and 39 per cent of combustible gases. Farkas and Wansbrough-Jones [10] find that undissociated formic, acetic and succinic acids in aqueous solution undergo several simultaneous photochemical changes. One is the direct formation of carbon dioxide and a hydrocarbon by a process analogous to that

[1] Kailan, A., *Monatsh.*, **34**, 1209 (1913).

[2] Ley, H., and Arends, B., *Z. physik. Chem.*, **B4**, 234 (1929); **B17**, 177 (1932); Price, W. C., and Evans, W. M., *Proc. Roy. Soc.*, **A162**, 110 (1937); earlier observations are due to Hantzsch, A., and von Halban, H., *Z. Elektrochem.*, **29**, 221 (1923).

[3] Ramsperger, H. C., and Porter, C. W., *J. Am. Chem. Soc.*, **48**, 1267 (1926).

[4] Harris, L., *Nature*, **118**, 482 (1926).

[5] Lederer, E. L., *Allgem. Öl.-u. Fettztg.*, **27**, 237 (1930); *Chem. Abs.*, **25**, 2014 (1931).

[6] Hartleb, O., *Strahlentherapie*, **39**, 442 (1931).

[7] Ley, H., and Hünecke, H., *Ber.*, **59**, 510 (1926).

[8] Herold, W., *Z. physik. Chem.*, **B18**, 265 (1932); *Z. Elektrochem.*, **38**, 633 (1932).

[9] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 68 (1913); *J. Soc. Chem. Ind.*, **29**, 1081 (1911).

[10] Farkas, L., and Wansbrough-Jones, O. H., *Z. physik. Chem.*, **B18**, 124 (1932).

encountered in the photochemistry of the ketones, $RCOOH + h\nu \rightarrow CO_2 + RH$. With acetic and propionic acids, the reaction, $RCOOH(H_2O) + h\nu \rightarrow CO + H_2O + ROH$ occurs (in aqueous solution) about 60 per cent as frequently as the reaction yielding carbon dioxide. Longer-chained acids tend, as do the aldehydes, to yield some unsaturated hydrocarbon and a shorter-chained acid: $CH_3CH_2CH_2COOH + h\nu \rightarrow C_2H_4 + CH_3COOH$. All of the acids yield condensation products.

In acetic acid vapor, which shows only a continuous spectrum, the chief reaction is dissociation into carbon dioxide and methane. The quantum yield (1850-2300A) is 0.45 for acetic acid, 1.0 for propionic acid and 0.4 for succinic acid. When polymers of the acids are present, the reaction is more complex. (See formic acid.) When acetic acid is decomposed in hexane solution, the solvent is attacked.

Burton,[11] using the mirror method, has found that hydrogen atoms but not methyl radicals are formed in the photolysis of acetic acid. Terenin[12] has also detected the hydroxyl radical in photolyses at about 1560A. To account for these results, Burton suggested two possible mechanisms, one being:

$$CH_3COOH + h\nu \longrightarrow CH_3COOH^*$$
$$CH_3COOH^* \longrightarrow CH_3COO + H$$
$$CH_3COO + H \longrightarrow CH_4 + CO_2$$
$$CH_3COOH + H \longrightarrow CH_4 + COOH$$
$$COOH \longrightarrow CO + OH$$
$$CH_3COOH + OH \longrightarrow CH_3COO + H_2O$$
$$2CH_3COO \longrightarrow C_2H_6 + 2CO_2.$$

In aqueous solutions of salts of aliphatic acids the decomposition is even more complex and, according to Jaeger and Berger,[13] is dependent upon the acid anion and other ions which may be present, particularly cations. According to Farkas and Wansbrough-Jones, the reaction depends upon absorption within the electron affinity spectrum of the anion by the process: $A'(H_2O) + h\nu \rightarrow A + OH' + H$, but because of a subsequent reaction $A + H \rightarrow A' + H^+$, the yield of the decomposition products is small. Addition of alkali favors the evolution of hydrogen and the formation of acids of higher basicity. Farkas states[14] the quantum yield of the reaction of the primarily produced hydrogen atom with acetate ion to form methane and carbon dioxide is 0.05 at pH 8.5. When silver acetate is used the hydrogen atoms may react with silver ions, so that the usual retarding process is less effective.

Acetic acid and aniline[15] in equimolar proportions when exposed to ultraviolet rays for 24 hours give nearly a 100 per cent yield of acetanilide. Propionic and benzoic acids act similarly. The yield of propionanilide is about 65 per cent of theoretical and that of benzanilide considerably less. Amide formation occurs much less readily, ammonium acetate in the presence of excess ammonium hydroxide giving only about 5.3 per cent acetamide, and ammonium benzoate even less benzamide.

[11] Burton, M., *J. Am. Chem. Soc.*, **58**, 692, 1645 (1936). Data for the photolysis of propionic acid have been given by Henkin, H., and Burton, M., *Ibid.*, **60**, 831 (1938). As in acetic acid, both hydrogen atoms and ultimate molecules are produced in primary processes. The relative number of hydrogen atoms per einstein is greater than in acetic acid.

[12] Terenin, A., *Acta Physicochim. U.R.S.S.*, **3**, 181 (1935).

[13] Jaeger, F. M., and Berger, G., *J. Chem. Soc.*, **119**, 2070 (1921); *Proc. Roy. Soc.*, **23**, 84 (1920).

[14] Farkas, L., *Z. physik. Chem.*, **B23**, 89 (1933).

[15] Stoermer, R., and Robert, E., *Ber.*, **55B**, 1030 (1922).

dl-α-Iodopropionic acid soon becomes colored by free iodine in daylight, and loses its iodine more rapidly in direct sunlight, or in chloroform solution in glass.[16]

Formic Acid[17]

Ramsperger and Porter[18] accomplished the complete decomposition of formic acid vapor by exposing the acid for 16 hours at a distance of 20 cm. from a 220-volt mercury arc at 20°C. Carbon monoxide and water constituted 64 per cent, and carbon dioxide and hydrogen, 36 per cent, of the mixed products formed by two photolytic processes. Müller and Hentschel[19] believed that some of the hydrogen formed reduces the acid further. Although the formation of methanol and formaldehyde could not be established, a noncrystalline solid was observed to form in the solution. They found also that the decomposition could be catalyzed by finely dispersed platinum.

Double molecules of formic acid present in the vapor phase decompose almost entirely to carbon dioxide and hydrogen.[20] The single molecules yield both these products and carbon monoxide and water, the ratio varying with the temperature and wave-length employed. At 40°C. and 2540A, the ratio is approximately 75.5 per cent carbon monoxide and water to 24.5 per cent carbon dioxide and hydrogen. At 100°C. and with the same wave-length, the amounts are 69 and 31 per cent, respectively. At shorter wave-lengths, 2100 and 1900A, the ratio is 42 per cent to 58 per cent. At these two latter wave-lengths, the quantum yield is unity for the decomposition of either double or single molecules.

An application of the para-hydrogen conversion test for atomic hydrogen showed only minimal formation of hydrogen atoms and carboxyl radicals, so that the primary process may consist in a rearrangement of bonds to give hydrogen and carbon dioxide directly. Burton[21] was unable to detect hydrogen atoms by the mirror test. Terenin,[22] however, detected OH by its emission spectrum when wave-lengths near 1560A were used.

According to Allmand and Reeve,[23] radiation of wave-length 3100A produces a slow decomposition of aqueous solutions of formic acid, the products being carbon dioxide and hydrogen, traces of formaldehyde and some more complex compound of highly reduced nature. The latter products were secured by reduction of formic acid by some of the hydrogen. In the presence of the uranyl ion, the decomposition in aqueous solutions is sensitized to visible light.[24] The velocity of photolysis depends upon the concentrations of the formic acid and the uranyl ion. With increasing concentrations of the latter, the velocity at first increases rapidly and passes through a maximum. The reaction is strongly desensitized by iodide, chloride and ferrous ions, hydroquinone, potassium dichromate, silver nitrate, sodium nitrite, potassium cyanide and mercuric sulfate, slightly desensitized by cupric sulfate, chromic sulfate,

[16] Hannerz, E., *Ber.*, **59B**, 1367 (1926).

[17] It has been claimed that methyl alcohol vapor and carbon monoxide exposed to ultraviolet rays or led over barium and potassium carbonates at 500°, give methyl formate and high-molecular compounds. Wietzel, G., and Wietzel, R., German P. 442,125, June 10, 1923, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **1928B**, 8.

[18] Ramsperger, H. C., and Porter, C. W., *J. Am. Chem. Soc.*, **48**, 1267 (1926).

[19] Müller, E., and Hentschel, H., *Ber.*, **59**, 1854 (1926).

[20] Gorin, E., and Taylor, H. S., *J. Am. Chem. Soc.*, **56**, 2042 (1934); see also Herr, W. N., and Noyes, W. A., Jr., *Ibid.*, **50**, 2345 (1928).

[21] Burton, M., *J. Am. Chem. Soc.*, **58**, 1655 (1936).

[22] Terenin, A., *Acta Physicochim. U.R.S.S.*, **3**, 181 (1935).

[23] Allmand, A. J., and Reeve, L., *J. Chem. Soc.*, 2852 (1926).

[24] Ouellet, C., *Helv. Chim. Acta*, **14**, 936 (1931); *Chem. Abs.*, **26**, 656 (1932); Büchi, P. F., [*Z. physik. Chem.*, **111**, 269 (1924)] gives the quantum yield as 0.7.

sodium nitrate and potassium fluoride. Photolysis is not affected by trisodium phosphate, ammonium acetate or magnesium sulfate. Oxidation-reduction properties of the desensitizer, which remains unchanged, play an important part in its effect. Increased concentration of the formic acid diminishes the effect of a desensitizer, but at 25 per cent concentration the velocity becomes almost independent of the concentration. When the concentration of the desensitizer is increased, the desensitizing effect increases rapidly at the beginning and then more slowly. Ghosh and Mitter [25] have given spectroscopic evidence for the formation of intermediate compounds of uranyl salts and organic acids.

A reaction in aqueous solution between sodium formate and iodine studied by Dhar and Bhargava [26] is unimolecular in darkness and "semimolecular" in light. Its velocity is proportional to the 0.75 to 0.66 power of the intensity of the incident light. It is a chain reaction, the quantum yield varying from 26 to 64, increasing with temperature and frequency of the light. More light is absorbed by the mixture than by the reactants separately.

Attention has been called to the formation of a peroxide from formic acid in the presence of oxygen, by short ultraviolet rays. The peroxide was assumed by Cantieni [27] to be performic acid.[28]

Relatively little work has been done on the photolysis of acetyl halides. The decomposition products contain carbon monoxide and the methyl halide, but no hydrogen, ethane or ethylene. The decomposition products from acetyl chloride contained hydrogen chloride and a polymer of either biacetyl or ketene. The products from acetyl bromide are bromine and $CH_2BrCH_2Br(?)$. Iodine is formed from acetyl iodide.[29]

The rates of decomposition of carbonyl hypohalites, *e.g.*, C_2H_5COOBr, are dependent both upon concentration and illumination, according to Bockemüller and Hoffmann,[30] daylight greatly retarding the decomposition.

Dibasic Acids

The photolysis of oxalic acid [31] consists in a primary decomposition into carbon dioxide and formic acid, followed by a secondary decomposition of the formic acid into carbon monoxide and hydrogen by rays of short wave-length. Kailan [32] concluded that the rate of the decomposition of dibasic acids increases with the duration of the exposure, but does not increase in proportion to the concentration of the acid. He found more carboxyl groups to be decomposed from malonic acid than from oxalic acid. Also, introduction of a hydroxyl group increased the rate of decomposition of dibasic acids. The rate of decomposition of malonic acid by sunlight in the presence of catalyst was found by Fay [33] to be exceedingly slow. Berthelot and Gaudechon [34] found uranyl salts to catalyze this

[25] Ghosh, J. C., and Mitter, B. N., *Quart. J. Indian Chem. Soc.*, **4**, 353 (1927); *Chem. Abs.*, **22**, 1899 (1928).

[26] Dhar, N. R., and Bhargava, P. N., *J. Phys. Chem.*, **39**, 1231 (1935).

[27] Cantieni, R., *Helv. Chim. Acta*, **19**, 1153 (1936); *Ber.*, **69B**, 1153 (1936). Similar behavior is shown by other fatty acids. *Z. wiss. Phot.*, **36**, 90 (1937); *Chem. Abs.*, **31**, 8381 (1937).

[28] Data on the decomposition of acetyl peroxide have been given by Walker, O. J., and Wild, G. L. E., *J. Chem. Soc.*, 1132 (1937).

[29] Etzler, D. H., and Rollefson, G. K., *J. Chem. Phys.*, **6**, 653 (1938).

[30] Bockemüller, W., and Hoffmann, F. W., *Ann.*, **520**, 165 (1935); *Chem. Abs.*, **29**, 7940 (1935).

[31] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **158**, 1791 (1914).

[32] Kailan, A., *Monatsh.*, **34**, 1209 (1913).

[33] Fay, H., *Am. Chem. J.*, **18**, 269 (1896).

[34] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **157**, 333 (1913).

reaction, and Volmar [35] found the main products of decomposition to be acetic acid and carbon dioxide.

Volmar also subjected a series of dibasic acids in 0.01 molar solutions to the light of a quartz mercury arc. Oxalic and malonic acids yields formic and acetic acids, respectively. Succinic acid gave a trace of propionic acid, but glutaric acid gave no butyric acid and liberated only 0.13 cc. of carbon dioxide in four hours. Oxalic acid, like formic acid, has the maximum sensitivity of the corresponding series of acids and has an absorption maximum at 2500A.[36] As the chain between the carboxyl groups lengthens, their mutual influence diminishes and from succinic acid onwards the groups behave as though they were independent.

Noyes and Kouperman [37] found a long induction period for the photolysis of solid oxalic acid by wave-lengths shorter than 2500A. Following the induction period, the rate of decomposition attained a practically constant rate. This rate was apparently greater when short wave-lengths were employed. Their explanation was that such radiations might endow the decomposition products with an excess of kinetic energy which would aid their more rapid diffusion out from the interior of the crystals. The rate of thermal decomposition of solid silver oxalate may be increased by a previous exposure of the salt to light of wave-lengths less than 5200A.[38]

It was reported by Noyes and Kouperman that the rate of decomposition of oxalic acid was greater when the acid was in aqueous solution than when the acid was used alone. Allmand and Reeve [39] found the decomposition products of such solutions to be predominantly carbon dioxide, with small amounts of formaldehyde.[40] Wave-lengths as long as 3000A were effective in causing photolysis. In all cases, the quantum yields were low, but appeared to increase on dilution of the solution. For a 0.68 molar solution, 100 quanta were absorbed per molecule decomposed at 2650A, 2450 at 3000A and 1060 at 3650A.

Winther and Oxholt-Howe [41] found the quantum sensitivity of the decomposition of iron oxalate, succinate, tartrate, citrate and acetate for short wave-lengths to be greater than unity. Kunz-Krause and Manicke [42] reported that under the catalytic action of ferric chloride, 5.3 per cent of crystalline oxalic acid suffers decomposition after a five-hour arc light exposure and 61.7 per cent after 16 hours. Padoa and Vita [43] studied the action of light on the reaction

$$2FeCl_3 + H_2C_2O_4 \longrightarrow 2FeCl_2 + 2HCl + 2CO_2.$$

They believed that the sum of the effects obtained in the blue and violet regions is 1.123 times that of white light. In the presence of quinine bisulfate, the zone of active radiations was widened and the sum of the effects of blue, green and violet lights was said to be 2.125 times that of white light.

Complex Oxalate Ions. The quantities of potassium cobaltioxalate [44]

[35] Volmar, *Compt. rend.*, **180**, 1172 (1925).

[36] See Ley, H., and Arends, B., *Z. physik. Chem.*, **B17**, 177 (1932); Vlès, F., and Gex, M., *Compt. rend.*, **180**, 1342 (1923).

[37] Noyes, W. A., Jr., and Kouperman, A. B., *J. Am. Chem. Soc.*, **45**, 1398 (1923); Wobbe, D. E., and Noyes, W. A., Jr., *Ibid.*, **48**, 2856 (1926).

[38] Benton, A. F., and Cunningham, G. L., *J. Am. Chem. Soc.*, **57**, 2227 (1935).

[39] Allmand, A. J., and Reeve, L., *J. Chem. Soc.*, 2834 (1926).

[40] Baur, E., believes there is a direct decomposition into carbon monoxide, carbon dioxide and water. *Z. physik. Chem.*, **111**, 315 (1924).

[41] Winther, C., and Oxholt-Howe, H., *Z. wiss. Phot.*, **14**, 196 (1914).

[42] Kunz-Krause, H., and Manicke, P., *Ber. Pharm. Ges.*, **32**, 209 (1922).

[43] Padoa, M., and Vita, N., *Gazz. chim. ital.*, **54**, 147 (1924); see also *Atti Cong. naz. chim. pura applicata*, 398 (1923).

decomposed by the mercury arc in quartz vessels in identical intervals of time were approximately independent of the initial concentrations and determined chiefly by the light energy absorbed. The addition of alcohol had no appreciable effect, but neutral salts did have marked effects. Bhagwat and Dhar,[45] found the reaction to be greatly accelerated by short wave-length radiation. Also, the latter investigators gave the temperature coefficient of the thermal reaction as 3.7. In incandescent light, the coefficient was 1.85 and in sunlight 1.13. In sunlight the velocity was proportional to the square root of the light intensity, but in lamp light it was directly proportional to the intensity. Murgulescu[46] also finds the decomposition of 0.02-0.002 molar potassium cobaltioxalate by light of wave-lengths 4360, 4050, 3660 and 3130A to be of zero order.

$$[Co(C_2O_4)_3]''' + h\nu \longrightarrow [CO(C_2O_4)_2]'' + (C_2O_4)'$$

$$[Co(C_2O_4)_3]''' + (C_2O_4)' \longrightarrow (C_2O_4)'' + 2CO_2 + [Co(C_2O_4)_2]''$$

In most complex oxalates, Bhagwat[47] found the quantum yield to be two. He assumes the formation of an activated molecule as the primary process. On collision of this activated molecule with an unexcited molecule, both are decomposed. Potassium cuprioxalate requires a sensitizer in visible light. The decomposition products include copper, cuprous oxide, carbon monoxide and carbon dioxide. The quantum yield is 0.66. Bhagwat makes the assumption that the molecule absorbs two quanta before being further activated through the sensitizer. The sensitizers employed by Dube and Dhar[48] were ferric chloride or uranyl nitrate. The reaction was of zero order. Increasing the amount of the sensitizer increased the rate through a maximum. The reaction was more effectively retarded by oxygen than by carbon dioxide. It was accelerated by the presence of a large excess of potassium oxalate.

Potassium manganioxalate absorbs light throughout the visible, with a maximum at about 4870A. Ghosh and Kappanna[49] find white light to more than treble the velocity of thermal decomposition of the potassium complex. The quantum yield is one when plane polarized light is used. Addition of oxalic acid diminishes the velocity of the reaction.

Allmand and Webb[50] found in the photodecomposition of $K_3Fe(C_2O_4)_3$, that the quantum yields, which decrease with increasing wave-length, are of the order of unity. The presence of potassium oxalate caused a slight decrease in the quantum yield, but all other electrolytes tested increased the yield slightly. Experiments with mixed light with varying proportions of two or three mercury arc lines, showed an amount of decomposition 25 to 30 per cent greater than that calculated on the basis of an additivity of their separate effects. On the other hand, the use of a continuous band between 3900 and 4600A caused a degree of decomposition about 20 per cent lower than that expected on the basis of additivity. The effects of intermittent and continuous exposures were the same. The quantum yield was independent of the intensity of the line 3650A (in some experiments 4050A) over a range of fifteen to one, whether continuous or intermittent. These results tended to confirm the work of Padoa and Vita (see Chapter 12). They suggested that the primary result of the absorption of a light quantum is the activation of the ferrioxalate ion, a process regarded as involving the partial dislocation of the union between the ferric ion and one of the attached oxalate ions. Reaction then occurs on collision of such an activated ion with a normal ion. More recently, Allmand and Young[51] confirmed the synergistic action of two monochromatic rays and showed that the temperature coefficient for this reaction is "negative." They also observed that in aqueous solutions, the velocity of the photoreduction of ferric chloride by oxalic acid is proportional to the intensity, that the ferric ion has no effect other than a slight light filter effect, and that the quantum efficiency is of the order of unity.[52] Kornfeld and Mencke[53] had found the velocity proportional to the square root of the intensity of light in the blue, green, and violet and, within limits, independent of the concentration of the reagents. It varies with the duration of the reaction and rapidly tends to drop to zero. Addition of ferrous sulfate retards the reaction at a rate proportional to the concentration of the sulfate.

The decomposition of oxalic acid can also be sensitized to light by chromium and by uranyl salts, the latter being about three times as effective as the former.[54] The reaction in the presence of uranyl salts has been suggested for standardizing light sources employed in determination of the light fastness of dyes.[55] Büchi,[56] who finds the quantum yield to be unity, attributes the reaction to the decomposition of the non-ionized molecules of uranyl oxalate ($UO_2C_2O_4$) or of the complex ions $(UO_2(C_2O_4)_2)''$, since the rate is only independent of the oxalic acid concentration when the latter is equimolar with or greater than the uranyl salt.

Müller[57] disagrees with the theory of the formation of a sensitizer-complex molecule and attributes the decomposition to collisions of the second kind between activated uranyl ions and oxalic acid molecules or oxalate ions. Pierce[58] confirmed Bruner and Kozak[59] and Bacon[60] in finding a temperature coefficient of unity, but was unable to decide between the mechanisms involving a sensitizer-complex and that of Müller. Pringsheim[61] discards the theory of collisions with activated molecules because he finds the inhibiting effect of iodide ions on the photolysis too small in comparison with their effect on fluorescence. He therefore favors complex formation. The solution must not be alkaline when intended for use in an actinometer. The application of the reaction for this purpose has been discussed in Chapter 7, where more recent quantum yield measurements are mentioned.

The Eder Reaction. A reaction formerly employed in actinometry, but really too complex and too subject to the presence of accelerating and inhibiting impu-

[44] Berger, G., *Rec. trav. chim.*, **44**, 47 (1925); Jaeger, M., and Berger, G., *Proc. K. Akad. Wetensch. Amsterdam.*, **23**, 84 (1920); *J. Chem. Soc.*, **118**, ii, 725 (1920).

[45] Bhagwat, W. V., and Dhar, N. R., *Z. anorg. Chem.*, **197**, 18 (1931); *Brit. Chem. Abs.*, **1931A**, 579.

[46] Murgulescu, I. G., *Bul. soc. stiinte Cluj*, **8**, 193 (1935); *Chem. Abs.*, **30**, 4402 (1936).

[47] Bhagwat, W. V., *Z. anorg. allgem. Chem.*, **218**, 365 (1934); *Chem. Abs.*, **28**, 6636 (1934).

[48] Dube, H. L., and Dhar, N. R., *J. Phys. Chem.*, **36**, 626 (1932).

[49] Ghosh, J. C., and Kappanna, A. N., *Quart. J. Indian Chem. Soc.*, **3**, 127 (1926); *Brit. Chem. Abs.*, **A**, 1014 (1926).

[50] Allmand, A. J., and Webb, W. W., *J. Chem. Soc.*, 1518, 1531 (1929).

[51] Allmand, A. J., and Young, K. W., *J. Chem. Soc.*, 3079 (1931).

[52] See also Baur, E., Ouellet, C., and Wäckerlin, E., *Z. wiss. Phot.*, **30**, 88 (1931); *Chem. Abs.*, **26**, 3729 (1932).

[53] Kornfeld, G., and Mencke, E., *Z. Elektrochem.*, **34**, 598 (1928).

[54] Landau, M., *Compt. rend.*, **156**, 1894 (1913); Mathews, J. H., and Dewey, L. H., *J. Phys. Chem.*, **17**, 211 (1913); Boll, *J. Chem. Soc.*, **108**, ii, 123 (1925); Kunz-Krause, H., and Manicke, P., *Ber. pharm. Ges.*, **32**, 209 (1922); Sandonnini, C., *Atti accad. Lincei*, **2**, 427 (1925); *Chem. Abs.*, **20**, 1018 (1926).

[55] Holmes, W. C., *Amer. Dyestuff Rep.*, **13**, 188, 197 (1924); *Chem. Abs.*, **18**, 1614 (1924).

[56] Büchi, P. F., *Z. physik. Chem.*, **111**, 269 (1924); *Chem. Abs.*, **19**, 1097 (1925); Baur, E., *Z. physik. Chem.*, **111**, 315 (1924).

[57] Müller, R. H., *Proc. Roy. Soc.*, **121A**, 313 (1929).

[58] Pierce, W. C., *J. Am. Chem. Soc.*, **51**, 2731 (1929).

[59] Bruner, L., and Kozak, J., *Z. Elektrochem.*, **17**, 355 (1911).

[60] Bacon, R. E., *Philippine J. Sci.*, **2**, 129 (1907); **5**, 281 (1910).

[61] Pringsheim, P., *Physica*, **4**, 733 (1937); *Chem. Abs.*, **31**, 8380 (1937).

rities, is the Eder reaction.[62] A solution containing mercuric chloride and ammonium oxalate is employed. On exposure to light, the decomposition products of the oxalate were thought to bring about the reduction of the mercury salt to calomel. Winther [63] found that the sensitiveness of the solution to visible light depended upon the presence of traces of a ferric salt. The rate of deposition of calomel was proportional to the iron content provided this did not exceed a very low value. An excess of ferric salt, however, retarded the reaction, particularly in the absence of dissolved oxygen. Furthermore, highly purified solutions were still decomposed by ultraviolet light, although not markedly by visible light.

Comparative experiments by Winther and Oxholt-Howe,[64] in which equal volumes of the filtrate from the calomel formed in a previous exposure and a fresh solution of the same composition were exposed to the influence of light under similar conditions, indicate that the initial photochemical action leads to the formation of some substance which acts as a powerful negative catalyst. This is also observed in the case of a purified Eder's solution to which eosin has been added as a sensitizer to the visible. In general, the effect becomes more marked as the intensity of the light increases. There is an appreciable loss of sensitivity if the eosin solution has been insolated before having been added to the Eder's solution. Velocity measurements of these reactions have been made by Shpolskii and Ivanova.[65]

Padoa and Minganti [66] have measured the temperature coefficients of the reaction at various wave-lengths. The reaction in green light was very slow and a small proportion of a dilute aqueous solution of tetrabromofluorescein was added as a sensitizer; the latter was also employed in some experiments with white light. The results were as follows: white light, 1.29; ultraviolet, 1.05; dark blue, 1.21; green with sensitizer, 1.75; white light with sensitizer, 1.50. Here it is apparent that the longer the wave-length, the higher the temperature coefficient. The effect of the sensitizer in raising the temperature coefficient with white light is attributed to the fact that the sensitizer gives preponderance to the action of the yellow and green rays, which have little activity when no sensitizing agent is present.

Trifonov [67] found that potassium mercuric oxalate can be decomposed by water and by light. Various workers, including Ghosh and Rangcharya,[68] have advanced evidence, in some cases spectrographic, for the formation of an intermediate compound in Eder's solution. Cartledge and Djang [69] find cobaltous salts alone to be much less effective in inducing the reaction than are ferrous salts. The former affect chiefly the dark reaction. The effect of the cobaltioxalate complex ion is essentially a pure catalysis in the light. The inhibiting effect of oxygen

[62] Krauss, F., and Berge, K., *J. Prakt. Chem.*, **136**, 257 (1933); see also Bekhterev, P., *J. Russ. Phys.-Chem. Soc.*, **57**, 161 (1925); *Chem. Abs.*, **20**, 2459 (1926); Pitzer, E. C., Gordon, N., and Wilson, D., *J. Am. Chem. Soc.*, **58**, 67 (1936); Wieland, H., and Zilg, W., *Annalen*, **530**, 1656 (1937); *Chem. Abs.*, **32**, 1656 (1938).

[63] Winther, C., *Z. wiss. Phot.*, **8**, 135, 197 (1910); **14**, 172 (1914); Berger, G., *Rec. trav. chim.*, **40**, 387 (1921); *Chem. Abs.*, **16**, 1175 (1922).

[64] Winther, C., and Oxholt-Howe, H., *Z. wiss. Phot.*, **13**, 89 (1913); *J. Chem. Soc.*, **106**, II, 10 (1914).

[65] Shpolskii, E., and Ivanova, E. N., *J. Phys. Chem. (U.S.S.R.)*, **6**, 133 (1935); *Nature*, **16**, 647 (1930); *Chem. Abs.*, **29**, 7809 (1935). For the effect of oxygen, see Shpolskii, E., and Iljina, A., *Acta Physicochim. U.R.S.S.*, **3**, 269 (1935); *Brit. Chem. Abs.*, **A**, 1214 (1936).

[66] Padoa, M., and Minganti, T., *Atti accad. Lincei*, **24** (V), ii, 97 (1915); *J. Chem. Soc.*, **108**, (ii), 719 (1915).

[67] Trifonov, N., *Mit. wiss.-tech. Arb. Republ. (Russ.)*, **13**, 72 (1924); *Chem. Zentr.*, 382 (1925).

[68] Ghosh, J. C., and Rangcharya, T. L. K., *J. Indian Chem. Soc.*, **5**, 569 (1928).

[69] Cartledge, G. H., and Djang, T. G., *J. Am. Chem. Soc.*, **55**, 3214 (1933).

is greatest with the catalyzed photolysis, less with that which is uncatalyzed and least on the photolysis of the cobaltioxalate ion alone.[70]

Air, oxygen, hydrogen peroxide and ozone each inhibit the Eder reaction when the latter is carried out in the light of the carbon arc.[71] The same is true of the reduction of ferric oxalate. Roseveare and Olson [72] and Oberhauser and Schormüller [73] consider the Eder reaction a chain reaction. Phenols also strongly depress the reaction, an effect attributed by Weber [74] to a deactivation of the activated molecules or ions which form in the primary process. The same is true also of the eosin-sensitized reaction. When the solutions are saturated with oxygen, however, the phenols can depress the reaction only by acting as internal filters. Weber also believes the photosensitive component of the (unsensitized) solution to be a complex compound.

In the presence of eosin and with approximately monochromatic light of wave-length 5200A, 5460 or 5760A, there is a short induction period, after which the reaction proceeds linearly with time.[75] The speed of reaction is proportional to the intensity of light, both in the case of white light and of monochromatic illumination. In the concentration interval 5×10^{-7} to 5×10^{-5} gm. per cc., the speed increases in proportion to the concentration, but between 3×10^{-5} and 10^{-4} gm. per cc. the speed is constant. At higher concentrations, the rate begins to decrease. The decrease of sensitization as well as the damping of fluorescence as functions of the concentration begin from the same sharp threshold. The rate of the reaction is proportional to the concentration of mercuric chloride and, above concentrations of 0.01 gm. per cc., is independent of the concentration of oxalate. Between 15° and 5°, the temperature coefficient is 2.6 and between 25° and 15°, 1.9. The energy of activation is between 10 and 15 kcal. Beginning at 30°, the dark reaction acquires a noticeable speed. For the wave-lengths 5470 and 5760A, the quantum yield was, in the presence of oxygen, 12.5, a correction being made for the energy lost as fluorescence.[76]

Reaction Between Iodine and Potassium Oxalate in Aqueous Solution. The photochemical reaction between iodine and potassium oxalate

$$I_2 + C_2O_4'' \longrightarrow 2I' + 2CO_2$$

has been the subject of much study.[77] Berthoud and Bellenot showed that the rate of reaction is proportional to the concentration of the oxalate ion and inversely to the concentration of the iodide ion. The latter exerts a retarding effect. The rate is also proportional to the square root of the light intensity and to a power of the titratable iodine concentration which varies between 0.5 and −0.5 depending upon the completeness of the absorption of the light, that is, upon the wave-length. When absorption is weak, as it is when red light is employed, the rate is directly proportional to the square root of the iodine concentration but when

[70] Cartledge, G. H., and Goldheim, S. L., *J. Am. Chem. Soc.*, **55**, 3583 (1933) have attempted a determination of the nature of the complexes formed in Eder's solution.

[71] Dunnicliff, H. B., and Joshi, J. N., *J. Indian Chem. Soc.*, **6**, 121 (1929); *Chem. Abs.*, **23**, 2887 (1929).

[72] Roseveare, W. E., and Olson, A. R., *J. Am. Chem. Soc.*, **51**, 1716 (1929); **52**, 2617 (1930).

[73] Oberhauser, F., and Schormüller, J., *Annalen*, **470**, 111 (1929).

[74] Weber, K., *Z. physik. Chem.*, **A169**, 224 (1934).

[75] Shpolskii, E. V., and Kolesnikova, N. I., *J. Phys. Chem. (U.S.S.R.)*, **5**, 1199 (1934); *Chem. Abs.*, **29**, 6145 (1935); *Brit. Chem. Abs.*, **A**, 809 (1936).

[76] For an analogous reaction between mercuric chloride and malic acid in the presence of various sensitizers, see Baur, E., *Helv. Chim. Acta*, **20**, 974 (1937).

[77] Mukerji, B. K., and Dhar, N. R., *Z. physik. Chem.*, **120**, 75 (1926); *Z. Elektrochem.*, **31**, 621 (1925); *Trans. Faraday Soc.*, **21**, 489 (1926); Berthoud, A., and Bellenot, H., *Helv. Chim. Acta*, **7**, 304 (1924); *J. Chim. Phys.*, **21**, 308 (1924).

absorption is complete as in blue light, the rate is inversely proportional to the square root of the iodine concentration. The results of Berthoud and Bellenot on the relation of the rate to the intensity were subsequently confirmed by others, who varied the intensity by more adequate methods than their sector device.[78] Bhagwat[79] believes this square root relation is not constant when the rate is varied over wide limits. Dhar, Bhattacharya and Mukerji[80] find the relation between the velocity and the light intensity to vary from one-third to approximately five-fourths when the wave-lengths employed are in the range 3340 to 8750A.

Berthoud and Bellenot accounted for their results in either red or blue light by a mechanism which involved the assumption that light dissociates iodine molecules but not the triiodide ion predominantly present in the solutions, which contained an excess of potassium iodide. Their mechanism involved the chain reactions

$$I + C_2O_4'' \longrightarrow I' + C_2O_4'$$
$$C_2O_4' + I_2 \longrightarrow 2CO_2 + I' + I$$

and the chain-breaking reactions

$$2I + I' \longrightarrow I_3'$$
$$I + I \longrightarrow I_2$$

From these reactions and the assumption of stationary states for the concentrations of iodine atoms and C_2O_4', it was possible to attain agreement with the experimental results for the reaction rates under varied conditions. They found quantum yields of 0.11 (4860A) with respect to the total energy absorbed or 3.2 with respect to that absorbed by I_2. With blue light larger values, quantum yields up to 25 were obtained, verifying the chain nature of the reaction.

The temperature coefficients determined by Allmand and Young and by the Indian workers were high, about 3.0; those of the thermal reaction were as high as 6.86. This indicated a high energy of activation for some partial process, a feature difficult to reconcile with the chains proposed by Berthoud and Bellenot. Other reactions of iodine solutions required the concept that the triiodide ion present is photochemically decomposed with the production of iodine atoms and possibly the hypothetical ion I_2'. It was found possible by Dickinson and Ravitz[81] to derive a mechanism from this concept of the primary process which also led to the experimental results of Berthoud and Bellenot. Such a mechanism was employed by Allmand and Young, who appended to their paper a discussion of the application of the mechanism to other photochemical oxidations by iodine. This mechanism has also been used by Griffith, McKeown and Winn[82] in their treatment of the analogous reactions between bromine and potassium oxalate. They conceived the action of the free halogen to be only that of an internal light filter. In their experimental work they considered also the case in which there is but little of the iodide ion in excess. Berthoud,[83] however, has reiterated that it is the iodine molecule which is dissociated.

[78] Briers, F., Chapman, D. L., and Walters, E., *J. Chem. Soc.*, **129**, 562 (1926); Allmand, A. J., and Young, K. W., *Trans. Faraday Soc.*, **27**, 515 (1931).

[79] Bhagwat, W. V., *J. Indian Chem. Soc.*, **10**, 649 (1933); *Brit. Chem. Abs.*, **1934A**, 156; *Chem. Abs.*, **28**, 1928 (1934).

[80] Dhar, N. R., Bhattacharya, A. K., and Mukerji, B., *Nature*, **131**, 840 (1933); *J. Indian Chem. Soc.*, **12**, 151 (1935); *Brit. Chem. Abs.*, **1935A**, 832; *Chem. Abs.*, **29**, 5351 (1935).

[81] Dickinson, R. G., and Ravitz, S. F., *J. Am. Chem. Soc.*, **52**, 4770 (1930).

[82] Griffith, R. O., McKeown, A., and Winn, A. G., *Trans. Faraday Soc.*, **29**, 369, 386 (1933).

[83] Berthoud, A., *Helv. Chim. Acta*, **16**, 393 (1933).

Abel and Schmidt[84] have found evidence for the occurrence of the intermediary compound, probably C_2O_4', the existence of which had been assumed in the earlier mechanisms and for which kinetic evidence had been given by Abel, Schmidt and Retter.[85] Its long life is indicated by an initial reaction rate increase and by the photochemical after-effect which had been studied by the intermittent sector method by Berthoud. (See Chapter 15.)

It may also be noted that Bhattacharya and Dhar[86] have proposed that the analogous bromine-oxalate reaction may proceed by way of excited molecules, since they believe it can be markedly accelerated by wave-lengths in the region of 7304A.

Malonic and Other Acids. The products of the photodecomposition of malonic acid, either in the presence or absence of uranyl sulfate, are acetic acid and carbon dioxide.[87] With 0.01 molar uranyl sulfate, the rate decreases with decreasing concentrations of malonic acid, being approximately proportional to the cube root of the concentration of the latter. In the absence of catalyst, the quantum yield varies between 0.68 and 0.81, being little affected by the wave-length. In the presence of catalyst it is lower, 0.27. The extent of ionization of the malonic acid does not affect the results. There may be two independent reactions, one due to the light absorbed by the malonic acid and the other to that absorbed by the catalyst, but there is no evidence for the formation of a complex between malonic acid and uranyl salts. The mechanism of the catalyzed reaction may involve the deactivation of excited uranyl sulfate molecules by collision with other uranyl sulfate or with malonic acid molecules. The temperature coefficient of the sensitized reaction is 1.13,[88] and that of the unsensitized reaction, 1.07.[89] Malonic anhydride (carbon suboxide, C_2O_3) is not appreciably affected by ultraviolet light.[90]

Coster and van der Ziel[91] have noted in the photochemical decomposition of monoalkylmalonic acids the formation of a substance that is not a fatty acid. This conclusion was drawn from study of its x-ray spectrum.

A uranyl salt-photosensitized reaction between succinic acid and methylene blue at 3600A is, after an initial induction period, of zero order with respect to the methylene blue. The rate is proportional to the incident intensity and independent of the pH. One-half of the collisions between excited uranyl ions and succinic acid molecules are believed to be effective.[92]

Sattler and Nicolet[93] find treatment of diethyl cyclopropane-1,1-dicarboxylate with bromine at 40° to 50°C. under mercury arc irradiation through quartz gives both $Br < \begin{matrix} CH_2 \\ CH_2 \end{matrix} > C(COOC_2H_5)_2$ and $Br\,CH_2 \cdot CH_2 \cdot CBr \cdot (COOC_2H_5)_2$, with relatively larger amounts of the latter than when no irradiation is used. Stoermer

[84] Abel, E., and Schmidt, H., *Naturwiss.*, **23**, 501 (1935).

[85] Abel, E., Schmidt, H., and Retter, K., *Z. physik. Chem.*, **163A**, 53 (1932); see also for the after-effect in the reaction between iodine and oxalic acid, Abel, E., Jokisch, R. Larisch, L., and Sassmann, H., *Z. Elektrochem.*, **43**, 629 (1937).

[86] Bhattacharya, A. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **6**, 523 (1929); *Chem. Abs.*, **24**, 1033 (1930); Bhattacharya, A. K., Prakash, O., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **196**, 26 (1931); **209**, 139 (1932).

[87] Pierce, W. C., Leviton, A., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **51**, 80 (1929).

[88] Pierce, W. C., *J. Am. Chem. Soc.*, **51**, 2731 (1929).

[89] Pierce, W. C., and Morey, G. H., *J. Am. Chem. Soc.*, **54**, 467 (1932).

[90] Edwards, M. J., and Williams, J. M., *J. Chem. Soc.*, 856 (1927).

[91] Coster, D., and van der Ziel, A., *Z. physik. Chem.*, **B20**, 385 (1933).

[92] Ghosh, J. C., Banerjee, T., and Bhatta, B., *Z. physik. Chem.*, **B32**, 163 (1936).

[93] Sattler, L., and Nicolet, B. H., *J. Am. Chem. Soc.*, **49**, 2066 (1927).

and Ladewig [94] discovered that when alcoholic solutions of *trans*-cyclopentane-1,2-dicarboxylic acid are exposed to the Uviol lamp, conversion into mono- and di-esters occurs. The expected transformation into the *cis* modifications did not take place.

Oxalyl chloride is slowly decomposed when irradiated with wave-lengths shorter than 3800A, the reaction being predominantly monomolecular with a low quantum yield.[95] The final products are phosgene and carbon monoxide, but it is believed that the initial products are chlorine and carbon monoxide. Two mechanisms are proposed for the effects of different wave-lengths. With short ones, the molecule breaks at the carbon-carbon bond, but with longer wave-lengths, a break at one of the carbon-chlorine bonds predominates.

Hydroxylic Acids

Volmar [96] found that hydroxy-acids and their salts undergo photolysis under the influence of ultraviolet rays, and to a lesser extent in sunlight. Tartaric acid in 1-per cent solution after three hours gave 3.5 cc. of gas composed of carbon dioxide 66 per cent, carbon monoxide 10 per cent, hydrogen 21 per cent, and hydrocarbons 3 per cent. The solution contained aldehydes and small quantities of a reducing substance of the nature of a sugar. In the presence of alkalies, the carbon monoxide was lessened or absent, owing to condensation with a portion of the hydrogen with production of the aldehydic substances. The homologs of tartaric acid behaved similarly. The decomposition may be accelerated by the presence of catalysts such as uranyl acetate or iron salts.[97]

Winther [98] finds the oxidation of citric, tartaric, lactic and oxalic acids to be insensitive to light.

In the presence of tartaric, lactic or mandelic acids as oxygen acceptors, the photochemical reduction of ferric chloride is of zero order.[99] With both mandelic acid and lactic acid, the life period of the excited ferric ion is of the order of 10^{-9} second. With tartaric acid, the reaction is complicated by the circumstance that the immediate product of the photoöxidation of the acid also reacts with ferric salts under the influence of light. In the case of mandelic acid, the quantum yield is unity at 4880A, but becomes nearly 1.4 at 3900A; with tartaric acid and lactic acid, it is nearly 0.5 at 4880A and 0.8 at 3900A. Oxygen has been found a negative catalyst in the photochemical oxidation of lactic acid by bromine water by Dunnicliff and Joshi.[100]

Lactic Acid. The decomposition of solid calcium lactate by ultraviolet light was found to give carbon monoxide, methane, ethane and hydrogen.[101] Baudisch [102] stated that lactic acid, repeatedly purified from its zinc salt, gave decisive reactions for acetaldehyde after about forty hours of irradiation followed by distillation. He could not detect methane, although Schanz had previously found

[94] Stoermer, R., and Ladewig, H., *Ber.*, **47,** 1803 (1914).
[95] Krauskopf, K. B., and Rollefson, G. K., *J. Am. Chem. Soc.*, **58,** 443 (1936).
[96] Volmar, *Compt. rend.*, **176,** 742 (1923); *J. Chem. Soc.*, **124,** (II), 279 (1923); *J.S.C.I.*, 42A, 423 (1923).
[97] Neuberg, C., *Biochem. Z.*, **39,** 158 (1912).
[98] Winther, C., *Z. physik. Chem.*, **A174,** 41 (1935).
[99] Ghosh, J. C., and Purkayastha, R. M., *J. Indian Chem. Soc.*, **6,** 827 (1929); *Chem. Abs.*, **24,** 2055 (1930).
[100] Dunnicliff, H. B., and Joshi, J. N., *J. Indian Chem. Soc.*, **6,** 121 (1929); *Chem. Abs.*, **23,** 2887 (1929).
[101] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151,** 478 (1910).
[102] Baudisch, O., *Biochem. Z.*, **103,** 59 (1920); *Chem. Abs.*, **14,** 2776 (1920).

a small amount.[103] Euler [104] had, however, previously shown that in pure aqueous solutions at 70°C., there were produced alcohol and a gas, the latter being 90 per cent carbon dioxide and 10 per cent a mixture of hydrogen and carbon monoxide. The rate did not appear to depend upon the concentration of the acid. An induction period of about two hours was noted. The rate of evolution of gas was not accelerated by the presence of either ferrous or ferric salts, although the latter were reduced.[105]

Bredig, Mangold and Williams [106] state that inactive lactic acid is decomposed by light of wave lengths 2200 to 3000A, but is not rendered optically active. Bolin [107] found that no decomposition occurs in glass flasks.[108] Burns [109] found wave lengths less than 2500A effective in decomposing lactic acid in aqueous solution, the chief products being alcohol and carbon dioxide. The amounts of alcohol were 19 per cent in excess of those required by the assumption that the products are equal amounts of alcohol and carbon dioxide. The quantum yield, based on the carbon dioxide, was approximately 0.65, although the intensity measurements were admittedly inaccurate. Based upon the alcohol formed, it was 0.77. Carbon monoxide, 3.82 per cent of the total gas, saturated hydrocarbons, 5.36 per cent and unsaturated hydrocarbons 0.89 per cent, formed about 9 per cent of the gaseous products, but neither aldehyde nor hydrogen peroxide could be detected. Lieben, Löwe, and Bauminger [110] have stated that lactic acid in alkaline solutions yields acetaldehyde and acetic acid, possibly formed through pyruvic acid, which in alkaline solution they found to be more readily attacked than lactic acid. The reaction could be sensitized to diffused daylight by sodium anthraquinonesulfonate. Müller [111] found that in the presence of uranyl sulfate, lactic acid and sodium lactate could be photochemically converted into acetaldehyde with a quantum yield of approximately unity (4025A).

Ganassini [112] and Ciamician and Silber [113] found that lactic acid on prolonged exposure to sunlight in the presence of air yielded qualitative tests for acetic acid, pyruvic acid, acetaldehyde and carbon dioxide. Burns,[114] in extending his work to oxygen-containing solutions, noted the chief products to be carbon dioxide, acetaldehyde, a peroxide and acetic acid, thus confirming the results of Baudisch and of Neuberg if it were assumed that they had worked without excluding oxygen. Neither ethanol nor pyruvic acid could be detected.

Studies of the rate of the oxidation of mandelic acid by methylene blue in the presence of uranyl nitrate as photosensitizer have been made by Ghosh, Narayanmurti and Roy [115] at 4360, 3660, 3130 and 2540A. In each case, there were short induction periods, those at 3660A, and particularly 4360A, being longer. The results

[103] Schanz, F., *Arch. ges. Physiol.*, **170,** 650 (1918).
[104] Euler, H., *Arkiv. Kem. Min. Geol.*, No. 8, 1911; *J. Chem. Soc.*, **102,** ii, 112 (1912). Euler, H., and Ryd, S., *Biochem. Z.*, **51,** 97 (1913); Euler, H., and Lindberg, E., *Ibid.*, **39,** 410 (1912).
[105] See also Schanz, F., *Arch. ges. Physiol.*, **170,** 650 (1918).
[106] Bredig, G., Mangold, P., and Williams, T. G., *Z. angew. Chem.*, **36,** 456 (1923); *Chem. Abs.*, **17,** 3868 (1923).
[107] Bolin, I., *Z. physik. Chem.*, **87,** 490 (1914).
[108] For absorption data, see Dietzel, R., and Krug, R., *Arch. Pharm.*, **264,** 117 (1926).
[109] Burns, G. R., *J. Am. Chem. Soc.*, **51,** 3165 (1929).
[110] Lieben, F., Löwe, L., and Bauminger, B., *Biochem. Z.*, **271,** 209 (1934).
[111] Müller, R. H., *Biochem. Z.*, **178,** 77 (1926).
[112] Ganassini, D., *Chem. Zentr.*, I, 387 (1913); I, 729 (1910); *Chem. Abs.*, **5,** 3236 (1911) from *Seduta soc. med. chir., Pavia,* 1909.
[113] Ciamician, G., and Silber, P., *Ber.*, **46,** 1558 (1913).
[114] Burns, G. R., *J. Am. Chem. Soc.*, **52,** 5272 (1930).
[115] Ghosh, J. C., Narayanmurti, D. S., and Roy, N. K., *Z. physik. Chem.*, **B29,** 236 (1935).

are complex. The photochemical oxidation of mandelic acid by bromine is of first order in the absence of potassium bromide and of zero order in its presence.[116]

Ghosh and Bhattacharya[117] find that for monochromatic light, the rate constant is proportional to the square root of the absorbed energy. It was believed that the combined action of rays of two wave-lengths was less than that of the sum of their effects taken separately. For 4360A the quantum yield is 12.5, but it varies greatly with the light intensity and wave-length.

Ghosh and Ray[118] find the uranyl-sensitized oxidation of mandelic acid by bromine a chain reaction with high quantum yield.

Tartaric Acid. The formation of reducing substances and carbon dioxide when tartaric acid is exposed to ultraviolet rays was described by Euler and Ryd.[119] Ferric salts increase the rate of gas evolution, being themselves reduced.[120] In the presence of uranium salts, the α-hydroxy acids decompose slowly in sunlight into formic acid and the respective aldehydes and ketones.[121] Tartaric acid yields glyoxal and citric acid yields acetone. This photochemical reaction could be employed for the detection of tartaric acid in a solution of citric acid. It appeared specific in that it was not given by any of the other aliphatic hydroxy-acids examined by Pavolino. After the addition of a uranium salt, the solution to be examined is exposed for at least thirty minutes to sunlight or to a light source of similar intensity. A few drops of phenylhydrazine or a corresponding quantity of a 5 per cent solution of its acetate are added. If tartaric acid was originally present, a yellow precipitate of phenylglyoxal osazone formed. Its color soon changed to wine red, probably because of the oxidative effect of the uranium salt.

Volmar[122] finds that solutions of potassium antimonyl tartrate and the corresponding compounds of arsenic, bismuth, copper and iron undergo decomposition on exposure to ultraviolet radiation with liberation of the metal, the maximum effect being produced in the case of the bismuth compound. Potassium borotartrate is an exception; Volmer considers this due to the fact that it appears to be a mixture rather than a definite compound.

Light accelerates the direct air oxidation of sodium tartrate catalyzed by sodium sulfite, cerium hydroxide, sodium hydroxide, sodium carbonate or bicarbonate and ferrous hydroxide.[123]

The oxidation of citric acid by chromic acid has temperature coefficients of 3.8 in darkness and 1.05 in light. The velocity varies as the square root of the light intensity, although in the case of tartaric and lactic acids, the rate is directly proportional to the light intensity.[124]

In the case of citric acid, the process involves chains, the length of which increases with temperature and concentration.

[116] Ghosh, J. C., and Purkayastha, R. M., *Z. physik. Chem.*, **7B**, 285 (1930); *J. Indian Chem. Soc.*, **6**, 361 (1929).

[117] Ghosh, J. C., and Bhattacharya, S. K., *Z. physik. Chem.*, **31B**, 420 (1936).

[118] Ghosh, J. C., and Ray, B. B., *Z. physik. Chem.*, **32B**, 158 (1936).

[119] Euler, H., and Ryd, S., *Biochem. Z.*, **51**, 97 (1913).

[120] For data on the absorption spectra of tartaric acid solutions, see Bruhat, G., and Legris, R., *Compt. rend.*, **189**, 745 (1929); *Ann. Phys.*, **13**, 6 (1930); Descamps, R., *Compt. rend.*, **185**, 116 (1927); Lucas, R., and Schwob, M., *Compt. rend.*, **192**, 225 (1931); Bruhat, G., *Compt. rend.*, **192**, 489 (1931).

[121] Pavolino, T., *Giorn. farm. chim.*, **79**, 310 (1930); *Chem. Abs.*, **25**, 251 (1931).

[122] Volmar, *Compt. rend.*, **176**, 1465 (1923); *J. Chem. Soc.*, **124** (ii), 453 (1923).

[123] Palit, C. C., and Dhar, N. R., *J. Indian Chem. Soc.*, **11**, 471 (1934); *Chem. Abs.*, **28**, 6780 (1934).

[124] Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **169**, 381 (1928); *Chem. Abs.*, **22**, 2111 (1928); *Z. anorg. allgem. Chem.*, **196**, 26 (1931); *Chem. Abs.*, **25**, 2052 (1931).

Keto-acids

Comparatively few photochemical studies have been made of the ketonic acids, although occasional use has been made of ultraviolet absorption studies in the solution of problems relating to their constitution.[125]

The yield of acetoin formed by ultraviolet light from aqueous solutions of pyruvic acid decreases from 100 per cent at 0.2 to 3 molar to 12 per cent at 11.4 molar.[126] In the presence of benzaldehyde, Discherl detected the formation of acetylphenylcarbinol. Benzaldehyde, benzene, salts and dehydrating agents hinder acyloin formation. The irradiation of 0.5 to 2 molar solutions of α-ketovaleric acid gave a 39 to 40 per cent yield of butyroin.

The photoöxidation of pyruvic acid is sensitized by eosin and isochlorophylline, slightly by rhodamine B and is inhibited by hydrogen cyanide. In alkaline solutions, oxalic acid is formed.[127] Lipmann[128] finds light to increase the reduction of methylene blue or of ferric ion by pyruvic acid. In the latter case, the pyruvic acid appeared to be oxidized to acetic acid and carbon dioxide.

When sensitized by eosin, chlorophyll, ferric or uranyl salts, the photochemical oxidation of glycolic acid yields formaldehyde and carbon dioxide, but glyoxylic acid gives only carbonic acid.[129] Ferric gluconate is reduced in sunlight to a ferrous salt.[130]

Halogenated Acids

Ultraviolet light splits aqueous solutions of halogenated fatty acids and their salts in various ways, among the products being formaldehyde, carbon dioxide, hydrogen, and chlorine.[131] Euler[132] found that the haloacetic acids split off their halogen in aqueous solutions at 18°C. in ultraviolet light at a rate comparable to that in darkness at 100°C. The rate decreased at higher concentrations of the acids.

In benzene solution, monochloracetic acid also lost some chlorine. Other products identified included a small amount of polyglycolide, fumaric acid and another unsaturated acid. Bromoacetic acid suffered decomposition more readily. Little is known of the mechanism by which the unsaturated acids were produced. In ether, qualitatively similar results were also reported with both monochlor- and monobrom-acetic acids. The reaction becomes evident when wave-lengths between 3130 and 2660A are employed. A quantum yield of unity at 2536A was reported by Rudberg[133] for monochloracetic acid. For monobromacetic acid, he found it only 0.34, but that this increased as the solution was made alkaline. More recently, Farkas[134] has reported for monochloracetic acid a quantum yield of 0.9, inde-

[125] Pyruvic acid, Henri V., and Fromageot, C., *Bull. soc. chim.*, **37**, 845 (1925); Pascal, P., *Ibid.*, **39**, 396 (1926); Benzylmethylglyoxal, Lowry, T. M., Moureau, H., and MacConkey, C. A., *J. Chem. Soc.*, 3167 (**1928**); Levulinic acid, Gex. M., *Arch. phys. biol.*, **10**, 250 (1933); α-ketonic acids, Fromageot, C. Pelletier, M., and Ehrenstein, P., *Bull. soc. chim.*, **51**, 1282 (1932); β-ketogluconic acid, Niederhoff, P., *Z. physiol. Chem.*, **181**, 83 (1929).

[126] Discherl, W., *Z. physiol. Chem.*, **219**, 177 (1933); *Brit. Chem. Abs.*, **1933A**, 1037.

[127] Meyer, K., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 341 (1935); *Chem. Abs.*, **30**, 7457 (1936).

[128] Lipmann, F., *Skand. Arch. Physiol.*, **76**, 186 (1937); *Chem. Abs.*, **31**, 4904 (1937).

[129] Baur, E., *Helv. Chim. Acta*, **19**, 234 (1936).

[130] Neiger, R., and Neuschul, P., *Z. physik. Chem.*, **A177**, 355 (1936).

[131] Jaeger, F. M., and Berger, G., *Rec. trav. chim.*, **41**, 71 (1922).

[132] Euler, H., *Ber.*, **49**, 1366 (1916).

[133] Rudberg, E. G., *Z. Physik*, **24**, 247 (1924).

[134] Farkas, L., *Z. physik. Chem.*, **B23**, 89 (1933).

pendent of the pH of the solution for wave-lengths less than 2300A. Dain and Puzenkin[135] employ the reaction for absolute actinometric measurements.

The photochemical reactions between the halo-acetic acids and alcohol were studied by Cassel,[136] who observed decomposition into the unsubstituted acid, acetic aldehyde and the halogen acid. Wave-lengths shorter than 2500A were required. The halogen could be more readily liberated by light from 1-bromosuccinic acid than from 1-chlorosuccinic acid.

A uranyl-sensitized photoöxidation of monochloracetic acid by potassium permanganate has been found of zero order with respect to the oxidant by Ghosh and Ray,[137] who employed the wave-lengths 3660 and 4360A. Its rate varies as the intensity of the incident radiation and is influenced by the sensitizer concentration.

Trichloracetic acid decomposes into carbon dioxide and chloroform, the temperature coefficient being 3.6 in light and 4.28 in darkness, according to Banerji and Dhar.[138] The quantum yields are abnormally high and increase with the temperature and the frequency of the incident radiation.[139] Solutions in water show some absorption of visible light which is without much photochemical effect, although water acts as photosensitizer. Absorption begins to increase at 3200A, is complete at 3000A, and decreases at shorter wave-lengths.

Unsaturated Acids

The stereoisomeric transformations of unsaturated dicarboxylic acids, direct and sensitized, have been much studied. Kailan[140] found that solid fumaric acid was not converted into maleic acid by ultraviolet light, and that maleic acid could be converted into fumaric only to the very slightest extent. But in aqueous solutions (about 0.084 normal), an equilibrium between the two acids could be reached from either side. The equilibrium was displaced somewhat toward the side of maleic acid with increasing concentrations. At 45° to 50°C., with 0.1*N* solution the equilibrium mixture contained 75 per cent of maleic acid and in 0.4*N* solution 79 per cent. The velocity of transformation was much greater in quartz than in glass vessels, but the equilibrium composition was the same.

Earlier observations were recorded by Stoermer with Frederici, Brautigam and Neckel,[141] who found that although fumaric acid when irradiated yielded about 70 per cent of maleic acid, sodium fumarate could not be converted into sodium maleate in this manner. The transformation of fumaric acid into maleic acid could also be effected in benzene solution.[142] Stoermer, who has made extensive investigations of the stereoisomeric transformations of ethenoid linkages in a wide variety of compounds, showed that at photochemical equilibrium, the less stable form was present in the larger amount, proving that light does not act merely as a catalyst in hastening a thermal equilibrium.

[135] Dain, B. Y., and Puzenkin, E. S., *Ber. ukrain. wiss. Forsch-Inst. physik. Chem.*, **4**, 75 (1934); *Chem. Abs.*, **29**, 2451 (1935).

[136] Cassel, H. W., *Z. physik. Chem.*, **92**, 113 (1916).

[137] Ghosh, J. C., and Ray, B. B., *J. Indian Chem. Soc.*, **13**, 1 (1936); *Chem. Abs.*, **30**, 4093 (1936).

[138] Banerji, S. N., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **134**, 172 (1924); *Chem. Abs.*, **18**, 2634 (1924).

[139] Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **209**, 123 (1932); *Chem. Abs.*, **27**, 907 (1933).

[140] Kailan, A., *Z. physik. Chem.*, **87**, 333 (1914); *J. Chem. Soc.*, **106** (ii), 449 (1914); *Monatsh.*, **41**, 305 (1920); *Chem. Abs.*, **15**, 1100 (1921).

[141] Stoermer, R., with Frederici, Brautigam, and Neckel, *Ber.*, **44**, 637 (1911).

[142] Stoermer, R., *Ber.*, **42**, 4865 (1909); *J. Chem. Soc.*, **98** (ii), 114 (1910).

Warburg[143] measured the quantum yields for the transformation of each stereoisomer at the wave-lengths 2070, 2530 and 2820A. The yields were but little affected by the change in wave-length, being slightly greater at 2530A than at either of the other two. For the conversion of maleic into fumaric acid, the values ranged from 0.032 to 0.049, being slightly greater at lower (0.00514) than at higher (0.0102) concentrations. For the reverse transformation of fumaric into maleic acid, the yields were about twice as great, varying from 0.08 to 0.133. In this case, the higher values were obtained in the more concentrated solutions. The low quantum yields were assumed to be due to the fact that after the initial excitation of the molecule, it tends on collision to return to the original form more frequently than it does to yield the isomer. At 3130A, Vaidya[144] found the quantum yields for maleic acid to be at 0.01 molar, 0.048, at 0.005 molar, 0.052 and for fumaric acid, 0.117 and 0.083, respectively.

Absorption data for maleic and fumaric acids, their *l*-menthyl and dimethyl esters and maleic anhydride in various solvents were given by Wassermann and Smakula[145] over the range 3000 to 1900A. Their data were thought not to eliminate the Anschütz cyclic formula for maleic acid.

It has been suggested that maleic and fumaric acids may have a common excited electronic state.[146] Olson[147] has given a theoretical treatment of the conversion. The potential energy wells corresponding to the separate acids are separated by a potential barrier, so that the transformation cannot occur thermally at ordinary temperatures. Olson plotted curves of the potential energy against the angle through which one half of the molecule is twisted relative to the other about the double bond as axis. Such curves for the excited state make evident the manner in which the stabilizing effect of the double bond disappears on excitation of one of the electrons of the bond. From these curves Olson determined by the methods of wave mechanics, the probabilities that on the return of the molecule from the excited state, the *cis* or the *trans* form would result. With Hudson, Olson[148] further developed methods for predicting from the extinction coefficients of the acids at various concentrations and wave-lengths, the compositions of the photostationary states when the acids, in several concentrations, are irradiated with various monochromatic wave-lengths. From thermal data, calculations of the heats of isomerization were also made.

Comparison of the absorption spectra of the *cis* and *trans* forms of a number of related stereoisomeric compounds usually show that of the more stable *trans* form to lie closer to the visible. Contrary to this general rule, in the three pairs of compounds, diethyl $\alpha\alpha'$-diphenylfumarate and maleate, dimethyl $\alpha\alpha'$-di-*m*-tolylfumarate and maleate, and dimethyl $\alpha\alpha'$-di-*p*-tolylfumarate and maleate, the absorption curve of the *cis* form is the closer to the visible, and is, therefore, the more stable form at low temperatures. Ramart-Lucas and Hoch[149] prepared these three fumarates by the irreversible action of ultraviolet on the corresponding maleates; this reaction gave, in addition, carbalkoxyarylindones, also formed by the action of ultraviolet light on the dialkyl $\alpha\alpha'$-diarylfumarates. Irradiation of the

[143] Warburg, E., *Sitzb. Preuss. Akad. Math.-Phys.*, 960 **(1919)**; *Chem. Abs.*, **14**, 1931 (1920).

[144] Vaidya, B. K., *Proc. Roy. Soc.*, **A129**, 299 (1930).

[145] Wassermann, A., and Smakula, A., *Z. physik. Chem.*, **A155**, 366 (1931).

[146] Bonhoeffer, K. F., and Harteck, P., "Grundlagen der Photochemie," Dresden, Steinkopff, 270, 1933.

[147] Olson, A. R., *Trans. Faraday Soc.*, **27**, 69 (1931).

[148] Olson, A. R., and Hudson, F. L., *J. Am. Chem. Soc.*, **55**, 1413 (1933).

[149] Ramart-Lucas, Mme., and Hoch, J., *Compt. rend.*, **189**, 696 (1929).

sodium salts of the $\alpha\alpha'$-diarylmaleic acids with ultraviolet light gave the sodium salts of the arylindonecarboxylic acid.[150]

The possibility of the photodissociation of the unsaturated acids into carbon dioxide and acids of the acrylic series has been discussed. Volmar[151] found that unsaturated dibasic acids undergo photolysis more rapidly than their saturated analogs. That of the *cis* compounds was five to six times as rapid as that of the *trans* forms, the latter behaving like monobasic acids. In the *cis* acids, the carboxyl groups were thought to exert a mutually enhancing effect. Itaconic acid behaved like succinic acid. On prolonged exposure to ultraviolet light, both the *cis* and *trans* forms behave alike after an equilibrium state has been set up. Olson and Hudson found that such photolyses occur with insufficient speed to interfere with their determinations of the stationary states resulting from stereoisomeric transformations.

Berezovskaya, Kogon and Moskalenskaya[152] found that light alone induced only the stereoisomeric changes in maleic and fumaric acids, but that the combined action of ultraviolet light and platinum led to decomposition. The barium salt of fumaric acid reacted similarly to the free acid, but the barium salt of maleic acid underwent no decomposition under these conditions.

The sensitization of the maleic-fumaric conversion to visible light by bromine, described by Wislicenus in 1895, has been extensively studied by Eggert and co-workers.[153] The ethyl esters were studied in carbon tetrachloride solution. The rate was proportional to the number of quanta absorbed, independent of the bromine concentration within the limits of 1:9, and independent of the carbon tetrachloride concentration within the limits 1:5. At 21°C., with the bromine concentration 0.1*N*, at the wave-length 4360A the quantum yield for the transformation was high, 295. At the same time, some of the bromine was photochemically added to the ester, the quantum yield for this reaction being 8.2.[154] These yields were independent of the intensity of the light and the concentration of the ester from pure ester to 70 moles of solvent per mole of ester. They were also independent of the bromine concentration from 0.03 to 0.3*N*. The intermediary formation of diethyl dibromosuccinate was postulated but no attempt was made to isolate it. Subsequent determinations by Wachholtz[155] at this wave-length showed, at various bromine concentrations, a range of from 108 to a maximum of 755 for the quantum yield for the transformation to fumarate. At 5570A the range was 77 to 307. The temperature and the wave-length employed were the chief determining factors. At the shorter wave-length (4360A) the yield increased approximately from 100 at 0° to 700 at 23°C.; at 5570A from 100 at 16° to 300 at 23°C. Similarly, the yields for the addition reaction depended only upon the temperature, wave-length and bromine concentration, values within the range of 3 to 42 being obtained. Bromine atoms, produced by photodissociation, form a complex short-lived intermediary product. This is considered a radical, since only one bromine atom is present. In a subsequent collision, the bromine atom is again liberated and fumarate formed. The liberation of the bromine permits it to act upon another maleate molecule and so accounts for the very high quantum

[150] See also Biquard, D., *Ann. Chim.*, **20**, 97 (1933), for the change of methyl diphenylmaleate to the fumarate on irradiation of its alcoholic solution, catalyzed by a trace of bromine.

[151] Volmar, *Compt. rend.*, **181**, 467 (1925).

[152] Berezovskaya, F. I., Kogon, M., and Moskalenskaya, E., *Compt. rend. acad. sci. U.R.S.S.*, **4**, 50 (1934); *Chem. Abs.*, **29**, 2089 (1935).

[153] Eggert, J., *Physik. Z.*, **24**, 504 (1923); *Chem. Abs.*, **18**, 3548 (1924).

[154] Eggert, J., Wachholtz, F., and Schmidt, R., *Physik. Z.*, **26**, 865 (1925).

[155] Wachholtz, F., *Z. physik. Chem.*, **125**, 1 (1927).

yields. In the event of a collision of the radical with a bromine molecule, it is possible that dibromosuccinic ester may be formed with liberation of a bromine atom.

In the case of the methyl ester (and also of the free acids), the quantum yields of the transformation and addition reactions are independent of the variation of the ester concentration and of the radiation intensity at high concentrations. At low concentrations, however, the yield for the isomerization decreases with decreasing ester concentration and with increasing intensity. Both this and the yield of the addition reaction are markedly dependent upon the temperature, as in the case of the ethyl ester.[156] The yield for the addition reaction depended upon the bromine concentration. The effect of change of wave-length (4360A, 5470A) is as follows: ethyl ester, ratio of yields at 4360 to 5470A, 1.9, methyl ester, 2.3. For the addition reaction, the corresponding values were 2.3 and 1.9. For free maleic acid, the ratio of the yields for the isomerization were 5:4:1, for ultraviolet, blue and green light.

In the system: maleic acid, sulfuric acid and bromine, at high concentrations of maleic acid, the transformation quantum yield is 430 at 21°C.[157] At lower concentrations of maleic acid, it is less, and becomes dependent on both the light intensity and the concentration of the maleic acid. The light reaction may, under these conditions, be initiated by the reduction of bromic acid, hypobromous acid and bromine. Reduction of bromine by ferrous sulfate gives a yield of 10,000 molecules of fumaric acid per atom of bromine formed. The yield is practically independent of the concentration of the reactants as long as the ferrous ion concentration is less than 10^{-5}, but at higher concentrations it becomes dependent on the ferrous ion concentration. These studies were undertaken to provide additional evidence that bromine atoms are responsible for the photosensitized conversion.[158]

The quantum yield of the addition of bromine to dimethyl fumarate is of the order of magnitude found by Wachholtz for the bromination of diethyl maleate or fumarate. It is not essentially different when aqueous solutions are used.

Mercuric bromide and mercurous nitrate and perchlorate are said also to sensitize the photochemical change of maleic to fumaric esters.

Stoermer and Robert[159] found the rearrangement of the amide of crotonic acid into that of isocrotonic acid to be easily effected by a Uviol lamp. By the aid of a Heraeus quartz lamp, they effected to some extent the conversion of the corresponding acid. Under the influence of ultraviolet light, it was also easily possible to secure the addition of the elements of water, methyl or ethyl alcohol to the double bond. Aniline and ammonia also add with the greatest ease at the double bond of α,β-unsaturated acids; crotonic acid and aniline give, together with a little of the anilides of crotonic and isocrotonic acids, chiefly $CH_3CH(NHC_6H_5)CH_2COOH$ and some of its anilide, while ammonia yields chiefly $CH_3CH(NH_2)CH_2COOH$ and iminodibutyric acid, with only very little of the amide of crotonic acid.

The separation of the two anilides is extraordinarily difficult and even on irradiating the pure stable anilide the amount of isoanilide obtained was not sufficient to permit of complete separation by careful fractional crystallization.

[156] Eggert, J., Wachholtz, F., and Schmidt, R., *Z. Elektrochem.*, **33**, 542 (1927).

[157] Wachholtz, F., *Z. Elektrochem.*, **33**, 542, 545 (1927).

[158] See also *Oesterr. Chem. Ztg.*, **30**, 110 (1927); *Z. physik. Chem.*, **135**, 147 (1928); Schmidt, R., *Z. physik. Chem.*, **B1**, 205 (1928).

[159] Stoermer, R., and Robert, E., *Ber.*, **55B**, 1030 (1922); *Chem. Abs.*, **8**, 2880 (1914); **16**, 3631 (1922).

With the Heraeus lamp the maximum rearrangement (40 per cent) of the amide of crotonic acid in acetone is attained in about two days. For the rearrangement of crotonic acid, toluene proved the best solvent.

Acrylic acid similarly treated with aniline gives $C_6H_5NHCH_2CH_2CONHC_6H_5$ and the deliquescent hydrochloride, melting about 64°C., of $C_6H_5NHCH_2CH_2COOC_2H_5$, a light yellow oil. From crotonic acid and paratoluidine was obtained ethyl *β-p*-toluidineobutyrate.

The conversion of the *α*-methylated mesaconic acid into citraconic acid is very difficult. In solution in water or methyl alcohol, the solvent appears to combine with the acid.[160] Quantum yields of 0.18 at 0.01 molar and 0.22 at 0.005 molar were reported by Vaidya[161] for 3130A for the isomerization of citraconic acid.

The acrylic acid esters prepared from glycerine, lactic acid, etc. when exposed to sunlight or ultraviolet light polymerize to varnish-like elastic masses. They are soluble in solvents for oils and are said to dry rapidly and not to be readily affected by exposure or by chemical agents.[162]

Malachowski and Maslowski[163] have prepared the *α*-, *β*-, and *γ-trans*-monomethyl esters of aconitic acid by irradiating the *cis* compounds in the presence of bromine by direct sunlight or a mercury arc.

Little, if any, work has been done on the photochemistry of the higher saturated fatty acids, but the long-chained unsaturated fatty acids have been frequently studied. The results of this work are discussed in Chapter 30 in connection with the behavior of drying oils.

Compounds Containing Nitrogen

Cyanogen Compounds. Hydrogen cyanide has no absorption spectrum between 2800A and 2100A but possesses a series of bands between 2001 and 1789A.[164] A few observations on the decomposition of hydrogen cyanide in cherry-laurel water have been reported by Andant and Rousseau.[165] They believed, since they found about as much (slight) decomposition to be effected by the 3650A line as by the total radiation of an arc to 3130A, that ultraviolet effects are nullified by the longer wave-lengths. They state that 0.126 gm. of manganese chloride in cherry-laurel water increases the action of ultraviolet rays so that the loss of hydrocyanic acid reaches 10.1 per cent in the first thirty minutes of irradiation and 30.0 per cent after two hours. They were inclined to attribute the activity to visible light.

Cyanogen is transformed into paracyanogen by ultraviolet rays.[166] On exposure to sunlight, cyanogen slowly polymerizes. In the presence of oxygen and ultraviolet light, it is oxidized completely to carbon dioxide and nitrogen. Hogness and Tsai,[167] observed in cyanogen gas at one atmosphere a series of diffuse bands beginning at 2240A and extending to the limits of dispersion of the quartz of their

[160] Stoermer, R., *Ber.*, **44**, 637 (1911).
[161] Vaidya, B. K., *Proc. Roy. Soc.*, **A129**, 299 (1930).
[162] Morrell, R. S., and de Waelle, A., "Rubber, Resins, Paints and Varnishes," New York, D. Van Nostrand Company, Inc., 1921.
[163] Malachowski, R., and Maslowski, M., *Ber.*, **61B**, 2521 (1928).
[164] Villars, D. S., *J. Am. Chem. Soc.*, **52**, 61 (1930); Hilgendorf, H. J., *Z. Physik*, **95**, 781 (1935).
[165] Andant, A., and Rousseau, E., *Compt. rend.*, **184**, 683, 1553 (1927); *Compt. rend. soc. biol.*, **96**, 613 (1927); *Chem. Abs.*, **21**, 3161 (1927).
[166] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1169 (1910); *J. Chem. Soc.*, **98**, ii, 349 (1910).
[167] Hogness, T. R., and Tsai, L. S., *J. Am. Chem. Soc.*, **54**, 123 (1932).

spectrograph. Their diffuse nature indicated the primary process to be one of predissociation, the available evidence indicating the products to be two CN molecules, one of which is excited.[168] The quantum efficiency for the polymerization by a hydrogen discharge source was found to be three. These authors were unable to confirm the observations of Berthelot and Gaudechon with the mercury arc, since cyanogen does not absorb any mercury lines.

Norrish and Smith[169] have described two reactions occurring when a mixture of nitric oxide and cyanogen is illuminated by radiations between 3600 and 2200A.

$$4NO \longrightarrow N_2 + 2NO_2.$$
$$4NO + (CN)_2 \longrightarrow 3N_2 + 2CO_2.$$

In the first of these, which occurs six times as extensively as the second, the cyanogen plays the part of a catalyst. Neither reaction occurs in the absence of a small amount of oxygen, which accumulates as the reaction proceeds, the effect being autocatalytic. The previously unknown molecule, NOCN, was suggested as an intermediary product.

A carbon tetrachloride solution of thiocyanogen $(SCN)_2$, according to Kaufmann and Liepe,[170] polymerizes readily in the sunlight. In ethereal solutions, substances having powerful odors are formed. Söderbäck[171] finds the addition of thiocyanogen to ethylenic hydrocarbons, which is very slow at ordinary temperatures, to go smoothly when the reactants are exposed in dry benzene solution to the action of actinic rays, yielding dithiocyanoethanes of the type CNS.CHR. CHR.CNS. Only two thiocyanogen radicals will combine with acetylenic hydrocarbons, giving compounds of the type CR′(CNS)=CR″CNS. Aromatic acetylene derivatives combine readily at the ordinary temperature in the dark, but aliphatic acetylenes require intense photocatalysis to cause addition. Interconversion of *cis* and *trans* forms under the influence of ultraviolet light occurs with the compounds obtained from acetylenes, a 0.02*N* solution of free thiocyanogen in benzene being an effective catalyst for the change. Acetylene itself yields a solid *s*-dithiocyanoethylene, melting 97-98.5°, and a liquid form, melting 15-17°, which are interconvertible under the influence of light.

Irradiation of fumaronitrile in acetone with ultraviolet light for 100 hours gives maleonitrile and an additive compound.[172]

Ganassini[173] finds that sunlight produces a yellow color in allylisothiocyanate and that, after a month, it deposits a precipitate. In the presence of water, decomposition occurs to the extent of 5 per cent and, in its absence, to the extent of 15 per cent, air being present in either case. He suggested the following possible reactions.

$$3C_3H_5NCS + 3H_2O \longrightarrow C_3H_5NH_2 + (C_3H_5)_2O + 2HCNS + H_2S + CO_2$$
$$9HCNS \longrightarrow 2(CNS)_3 + 3HCN + 3H_2S.$$

Sulfuric acid and ammonia are also formed by secondary reactions.

The polymerization of methylacrylonitrile in ultraviolet light has been described

[168] See also Mooney, R. B., and Reid, H. G., *Nature*, **128**, 271 (1931).
[169] Norrish, R. G. W., and Smith, F. F. P., *Trans. Faraday Soc.*, **24**, 620 (1928).
[170] Kaufmann, H. P., and Liepe, J.; *Ber.*, **56B**, 2514 (1923).
[171] Söderbäck, E., *Annalen*, **443**, 142 (1925).
[172] Jennen, J., *Bull. soc. chim. Belg.*, **46**, 258 (1937); *Brit. Chem. Abs.*, A II, 404 (1937); *Chem. Abs.*, **32**, 500 (1932).
[173] Ganassini, D., *Arch. ist. biochim. ital.*, **3**, 1 (1931); *Chem. Abs.*, **26**, 2657 (1932).

by Mertens and Fonteyn.[174] Considerable information has been obtained regarding the absorption spectra of the nitriles and amides of many acids.[175]

Amines. Dissolved in hexane, ammonia has a band at about 1920A, which is displaced toward shorter wave-lengths in aqueous solution.[176] Other amines exhibit similar solvent effects.

In the gaseous state, the amines exhibit a series of diffuse predissociation absorption bands, increasing in intensity toward the shorter wave-lengths, and attributed to an electronic excitation in the amino- group.[177] In methylamine the predissociation bands begin at 2440A and in ethylamine at 2370A.[178]

Berthelot and Gaudechon[179] found ethyl- and methylamine, guanidine, and hydroxylamine, when subjected to ultraviolet radiations, to be converted first into ammonia and then into nitrites. Emeléus and Jolley state that methylamine, on exposure to light from a mercury arc or an aluminum spark, produces equal amounts of ammonia and hydrogen and a liquid, with small quantities of methane and nitrogen. Ethylamine gives the same gaseous products and small quantities of ethane and ethylene. Benzene has also been found among the products.[180] Decomposition quantum yields of about 0.75 are found. The primary reaction is believed to form CH_3NH and H, rather than CH_3 and NH_2.[181] The photo-öxidation of methylamine yields principally ammonia; the quantum yield is again 0.75.

In the presence of zinc oxide, or titanium dioxide, the aliphatic amines are oxidized to nitrites in sunlight more readily than are the aromatic amino- derivatives. The amines are first hydrolyzed and then the ammonia is oxidized to nitrite and the alcohol to an aldehyde.[182]

Amides. Berthelot and Gaudechon[183] state that equal volumes of carbon monoxide and ammonia combine in a few hours to give formamide under the influence of rays of wave-length about 2000A to 3000A. Formamide also slowly decomposes when submitted to ultraviolet rays, the reaction being complicated by dehydration and formation of hydrogen cyanide. Light, less markedly than heat, produces polymerization.[184] The titanium dioxide-sensitized decomposition in sunlight proceeds more rapidly in the amides of monobasic than in those of dibasic acids.[185]

On exposure to ultraviolet rays[186] urea is said to be converted first into ammonia and then into a nitrite. Kailan,[187] however, found that a normal solution

[174] Mertens, E., and Fonteyn, M., *Bull. soc. chim. Belg.*, **45**, 438 (1936); *Chem. Abs.*, **30**, 8152 (1936).

[175] Bruylants, P., and Castille, A., *Bull. soc. chim. Belg.*, **34**, 261 (1925); Castille, A., and Gueurden, J., *Ann. soc. scient. Bruxelles*, **47B**, 56 (1927); Castille, A., and Ruppol, E., *Bull. sci. acad. roy. Belg.*, **16**, 1129 (1930); *Bull. soc. chim. Belg.*, **40**, 243 (1931); **44**, 351 (1935); Castille, A., *Bull. sci. acad. roy. Belg.*, **16**, 811 (1930); Ruppol, E., *Bull. sci. acad. roy. Belg.*, **21**, 236 (1935); Herzberg, G., and Scheibe, G., *Trans. Faraday Soc.*, **25**, 716 (1929).

[176] Ley, H., and Arends, B., *Z. physik. Chem.*, **B17**, 177 (1932); for the absorption of alkyl amines, see Ramart-Lucas, Mme., *Compt. rend.*, **194**, 726 (1932); Grunfeld, M., *Ibid.*, **194**, 1083 (1932).

[177] Herzberg, G., and Kölsch, R., *Z. Elektrochem.*, **39**, 572 (1933). Analyses of the methylamine bands have been given by Henri, V., and Lasareff, W., *Compt. rend.*, **200**, 829 (1935); *J. chim. phys.*, **32**, 353 (1935).

[178] Emeléus, H. J., and Jolley, L. J., *J. Chem. Soc.*, 1612 (1935).

[179] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 522 (1911).

[180] Emeléus, H. J., and Taylor, H. S., *J. Am. Chem. Soc.*, **53**, 2370 (1931).

[181] Emeléus, H. J., and Jolley, L. J., *loc. cit.*

[182] Rao, G. G., and Pandalai, K. M., *J. Indian Chem. Soc.*, **11**, 623 (1934); *Brit. Chem. Abs.*, **A** 1316 (1934).

[183] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 207 (1912).

[184] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1164 (1910); **151**, 478 (1910).

[185] Rao, G. G., and Pandalai, K. M., *J. Indian Chem. Soc.*, **11**, 623 (1934); *Chem. Abs.*, **29**, 1326 (1935).

[186] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 522 (1911).

[187] Kailan, A., *Z. physik. Chem.*, **95**, 215 (1920); *J. Chem. Soc.*, **118** (ii), 576 (1920).

of urea irradiated for 48 hours by a quartz mercury lamp (or for 1632 hours with the rays from 80 mg. of radium) showed no change in density, refractive index, or rate of change into ammonium cyanate, other than could be accounted for by experimental error.

Azomethane. This compound begins to absorb at about 4000A, exhibits a maximum at 3390A, a minimum at 2700A and increasing absorption at shorter wave-lengths. No evidence of definite bands appears.[188]

Ramsperger followed the photodecomposition by pressure measurements from which he concluded the reaction to be mainly

$$CH_3NNCH_3 \longrightarrow N_2 + C_2H_6.$$

He found the temperature coefficient to be about zero and the quantum yield two, the latter remaining practically constant over a two hundred-fold pressure range. To explain this result, Ramsperger made the assumption that the ethane molecule bore enough energy, derived from the heat of reaction and from the excess energy of the 3660A line employed over the energy required for the photodecomposition, to effect the decomposition of a second molecule of azomethane on collision with it. This theory would, however, be difficult to reconcile with the independence of the quantum yield and the pressure.

Since Ramsperger had used the "treacherous method of filters" in his quantum yield determinations, Forbes, Heidt and Sickman[189] repeated them, using for the energy determinations the uranyl oxalate actinometer. They made determinations at six wave-lengths of monochromatic light and at various pressures. At low pressures they found the quantum yield to approach unity as its upper limit, at least for the initial decomposition. It decreases with increasing decomposition at room temperature and also with increasing pressures. The latter points to a collisional deactivation. It was necessary in the measurements to use a graphical method of correcting for errors due to the deposition of difficultly volatile decomposition products upon the window. The quantum yields passed through a maximum in the region 3660 to 3350A, corresponding to the maximum of absorption by the N—N bond. At shorter wave-lengths they decreased, but began to increase again when wave-lengths absorbed by the N—C bond were employed. In agreement with Ramsperger, the temperature coefficient was zero at temperatures below 260°C.

That the decomposition is not a chain reaction between 20° and 226°C. was confirmed by Patat,[190] who believed the primary reaction to yield nitrogen and two methyl groups. His evidence for this was the fact that dimethyl ether at 150 to 600 mm. pressure could be decomposed in the presence of 10 to 30 mm. of irradiated azomethane. That the free methyl radicals did not form chains indicated the activation energy for the reaction between methyl and azomethane to be greater than 20 kcal. Burton, Davis and Taylor[191] believe quantum yield determinations based only on the pressure increase are too low. They find the amount of nitrogen produced in experiments at various temperatures always exceeds that of the hydrocarbons. The excess is a maximum at about 200°C. Methane increases and ethane decreases at the higher temperatures. The amount of higher

[188] Ramsperger, H. C., *J. Am. Chem. Soc.*, **50**, 123 (1928); for observations on azoisopropane, see *Proc. Nat. Acad. Sci.*, **13**, 849 (1927).

[189] Forbes, G. S., Heidt, L. J., and Sickman, D. V., *J. Am. Chem. Soc.*, **57**, 1935 (1935); see also Heidt, L. J., and Forbes, G. S., *Ibid.*, 2331.

[190] Patat, F., *Naturwiss.*, **23**, 801 (1935); *Nachr. ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe II*, [*N.F.*], **2**, 77 (1936); *Chem. Abs.*, **31**, 6112 (1937).

[191] Burton, M., Davis, T. W., and Taylor, H. A., *J. Am. Chem. Soc.*, **59**, 1038, 1989 (1937).

hydrocarbons increases with the degree of decomposition and with lowering of temperature. No hydrogen and only a little unsaturated hydrocarbon are produced. Burton, Davis and Taylor doubt that the temperature coefficient is zero below 226°C. They suggest the occurrence of a secondary association reaction between methyl radicals and $(CH_3N)_2$. When nitric oxide is present during photolysis, practically no alkane gas is produced.[192] From analyses of the reaction under these conditions, it is concluded that the source of ethane and other alkanes in the ordinary photolysis is not the combination of free radicals, but the decomposition of the association product with azomethane.

Diazo-Compounds. Diazomethane exhibits an absorption spectrum somewhat resembling that of azomethane.[193] It consists of a series of weak diffuse bands in the region 4710 to 4250A, followed by a continuum from 4250 to 3200A, and a second completely continuous region beginning at 2650A. The photochemical decomposition is unimolecular; the main products are nitrogen, ethylene, ethane and a non-volatile liquid. The quantum yield is approximately four at 3650 and 4360A. The primary process is the decomposition: $CH_2N_2 + h\nu \rightarrow CH_2 + N_2$. This is supported by the behavior of mixtures of the gas with hydrogen and with oxygen.

Adamson and Kenner[194] find that vinyldiazomethane, $CH_2{=}CHCH{=}N_2$, in 0.5-per cent ether solution forms pyrazole by a monomolecular photochemical reaction.

Ethyl diazoacetate, as such or in various solvents,[195] has an absorption curve similar to that of compounds containing a carbonyl group since both chromophores N=N and CO are said to have the same electron-term scheme. In the photolysis in heptane solution, the quantum yield rises from 0.20 for 4200A to 1.11 for 2600A; the rate of increase is small at first, but becomes greater in the band of shorter wave-length. In ethanol, methanol and water, there is a similar rise, but compared with heptane the values are smaller in the longer ultraviolet and greater in the shorter. For a given wave-length, the quantum yield either rises or falls in the order: heptane, ethanol, methanol, water. Neither a ten-fold increase in concentration nor a rise in temperature from 5° to 40°C. affects the quantum yield.

Goldfinger[196] measured manometrically photodecomposition by the full radiation of the mercury arc at various initial pressures from 0.04 to 297 mm. The relative velocity is greatest for the lowest pressure; the order of the reaction lies between zero and two. At low pressures, it is accelerated by argon. At higher pressures, it is retarded by nitrogen and by methane.

Nitro- Compounds. Chloropicrin is decomposed by violet or ultraviolet light, but the reaction soon stops because the nitrosyl chloride formed acts as an internal filter.

$$Cl_3CNO_2 + h\nu \longrightarrow NOCl + COCl_2.^{197}$$

According to Thompson and Purkis[198] methyl nitrite yields on photolysis a solid containing paraformaldehyde and formic acid, with small amounts of carbon

[192] Davis, T. W., Jahn, F. P., and Burton, M., *J. Am. Chem. Soc.*, **60**, 10 (1938).
[193] Kirkbride, F. W., and Norrish, R. G. W., *J. Chem. Soc.*, 119 (1933).
[194] Adamson, D. W., and Kenner, J., *J. Chem. Soc.*, 286 (1935).
[195] Wolf, E., *Z. physik. Chem.*, **B17**, 46 (1932).
[196] Goldfinger, G., *Compt. rend.*, **202**, 1502 (1936).
[197] Radulescu, D., and Zamfirescu, G., *Bul. soc. chim. Romania*, **17**, 87 (1935); *Chem. Abs.*, **30**, 671; see also Piutti, A., *Atti I Congr. naz. Chim. pura applicata*, 437 (1923); *J. Chem. Soc.*, **120**, 298 (1921); Piutti, A., and Mazza, F. P., *Gaz. chim. ital.*, **57**, 610 (1927); Alekseevskiĭ, E. V., *J. gen. Chem. (U.S.S.R.)*, **2**, 341 (1932).

monoxide and hydrogen, and 45 per cent each of nitrogen and nitrous oxide. In the case of ethyl nitrite, the volume decrease is less and the fraction of non-condensible gases is larger. Aldehydes are present in a liquid residue. The residual gas has 38 per cent of nitrogen, 30 per cent of nitrous oxide, 18 per cent of carbon monoxide and 13 per cent of methane.

In the wave-length range 2000 to 3000A, the primary process is believed[199] to be in the case of nitro-compounds

$$RCH_2NO_2 + h\nu \longrightarrow RCHO + NOH$$

This is followed by certain reactions of NOH and by oxidation of the aldehyde.

It is assumed that light absorbed by the molecule $R{-}CH_2{-}N\begin{matrix}O\\ \diagdown\!\!\diagup\\ O\end{matrix}$ changes it to the form $RCH{=}N\begin{matrix}OH\\ \diagdown\!\!\diagup\\ O\end{matrix}$, and that this is followed by a rupture of the molecule.

In the photolysis of tetramethylene nitrosochloride, the primary process, according to Hammick and Lister[200] is the elimination of NOH, the resulting olefin undergoing further reactions. The quantum yield is approximately unity. If the carbon atom to which the NO group is attached is also linked to an atom other than carbon, a photoöxidation occurs in the presence of oxygen with unit quantum efficiency. In the absence of oxygen, 1-chloro-1-nitroso-cyclohexane undergoes a rapid photoreaction without the evolution of gas. Red light decomposes nitroso-isopropylacetone to $H_2N_2O_2$ and its decomposition products and mesityl oxide. β-nitroso-β,ϵ-dimethylhexane probably gives a β,ϵ-dimethylhexene.[201]

Milone[202] finds ultraviolet irradiation to isomerize the α- and γ-forms of certain glyoximes, both in the solid state and in dilute alcohol, at 18°C., to the β-forms. The isomerization is also promoted very slowly by sunlight, but Wood light (3650A) is ineffective. Isomerization is more rapid in 30-40-per cent ethyl alcohol than in the solid state, as shown by the following data, which give the hours of exposure and the percentage of β-compound formed in solution and in the solid state, respectively: α-phenylglyoxime, 23,44.8; 17,20.7; α-*p*-tolylglyoxime, 22,28.8; 19,20.2; α-methylphenylglyoxime, 21,30.3; 19,15; α-diphenylglyoxime, 26,29; 20,15.9; γ-diphenylglyoxime, 28,41; 19,22.4. In sunlight, behind glass, γ-phenylglyoxime yielded only 0.93 per cent of the β-compound after 16 months.

After thirty minutes of exposure to ultraviolet rays, 0.10 gm. of nitroglycerin at 20 mm. gave 1.32 cc. of gas containing carbon dioxide, 24 per cent, carbon monoxide, 10.5 per cent, nitrogen, 17.5 per cent, nitrous oxide, 8.5 per cent and nitric oxide 39.5 per cent.[203] Some nitric oxide was destroyed in attacking the mercury in the testing apparatus. The high percentage of nitric oxide explains

[198] Thompson, H. W., and Purkis, C. H., *Trans. Faraday Soc.*, **32**, 674, 1466 (1936); for absorption data on nitrites and nitro-compounds, see also Goodeve, C. F., *Trans. Faraday Soc.*, **30**, 504 (1934); Kuhn, W., and Lehmann, H. L., *Z. physik. Chem.*, **18B**, 32 (1932).
[199] Hirschlaff, E. N., and Norrish, R. G. W., *J. Chem. Soc.*, 1580 (1936); see also Thompson, H. W., and Dainton, F. S., *Trans. Faraday Soc.*, **33**, 1546 (1937), for the decomposition of alkyl nitrites.
[200] Hammick, D. L., and Lister, M. W., *J. Chem. Soc.*, 489 (1937).
[201] Anderson, K. D., Crumpler, C. J., and Hammick, D. L., *J. Chem. Soc.*, 1679 (1935).
[202] Milone, M., *Gazz. chim. ital.*, **63**, 744 (1933); *Chem. Abs.*, **28**, 2713 (1934).
[203] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 201 (1912).

its presence in the products of decomposition of smokeless powders containing nitroglycerin.

Berthelot and Gaudechon[204] made this behavior the basis of a test for the stability of smokeless explosives. Samples were cut into cylinders weighing 0.25 to 0.45 g., placed over mercury in a quartz tube, containing nitrogen or carbon dioxide, and exposed to the radiations from a quartz mercury lamp at a distance of 78 to 80 mm. for six hours. Powders consisting only of nitrated cellulose were thought to be more stable than those containing nitroglycerin. An English Cordite containing 30 per cent of the latter and 5 per cent of Vaseline, exposed in one cubic centimeter of carbon dioxide, gave a mixture composed of the following volumes of gases: CO_2, 1 cc.; CO, 0.17 cc.; NO, 0.10 cc.; N_2O, 0.02 cc.; N_2, 0.10 cc. Results were also given for the French A and B powders and for Balistite of different ages and with stabilizers.

Experiments were also made in oxidizing (oxygen), reducing (hydrogen) and inert (carbon dioxide, nitrogen) atmospheres.[205] With oxygen, two-thirds of the free oxygen disappeared and added its oxidizing effect to that of the oxygen of the nitrocellulose. With hydrogen, about one-quarter disappeared, forming water and formaldehyde. With carbon dioxide, much depended on the temperature. At 25° to 30°C. (70 to 80 mm. from the lamp) there was absorption, due no doubt to the solvents and stabilizers which are basic in their character; at 40°C. (50 mm. distance) no change in volume occurred; at 75°C. (20 mm. distance) there was disengagement of carbon dioxide from the powder and the final volume showed an increase. Nitrogen had no effect on the evolution of nitrogen or nitrous gases from the powder.

Comparison[206] of two powders of the same age and make and stabilized by amyl alcohol and diphenylamine, respectively, showed that at 20 mm. (75°C.) amyl alcohol is the more efficient, the latter powder giving off less gas, and the gas containing a very much lower percentage of nitric oxide than the former. At 50 mm. (40°C.), on the other hand, diphenylamine is the more efficient stabilizer. Similar results were obtained with two naval powders, save that these evolved no nitrogen oxides. When the powders were treated with alkali (one gram with 20 cc. of 0.5*N* potassium hydroxide for 30 minutes at 15°C.), it was found that the diphenylamine powder showed less decomposition than that stabilized with amyl alcohol. A damaged naval powder, in which the brownish-yellow plates showed whitish stripes, was examined by the lamp. At both distances, the damaged part gave off more gas than the unaltered part, and this gas contained from 12 to 30 per cent of nitrogen oxide, while the gas from the unaltered part contained none.

A piece of nitrocellulose (collodion) 15 by 51.6 mm., after two hours at 20 mm., gave 0.87 cc. of gas, the percentages of its constituents being CO_2 25.5, CO 10.5, NO 39, N_2O 7, N_2 9.[207] Collodion, though less heavily nitrated than the French service smokeless powders, decomposed more readily and evolved a notable amount of nitric oxide.

Holmes and Patrick[208] stated that celluloid, when exposed to ultraviolet light, becomes brown and brittle with liberation of gaseous products, and that it not only absorbed liquid but the gel itself is decomposed by the rays. More recently,

[204] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **153**, 1220 (1911).
[205] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 514 (1912).
[206] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 201 (1912).
[207] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 201 (1912).
[208] Holmes, E. O., Jr., and Patrick, W. A., *J. Phys. Chem.*, **26**, 25 (1922).

however, Clément, Rivière and Beck[209] state that ultraviolet light does not exert a destructive effect on celluloids, or nitrocelluloses; instead, it seems to effect a molecular polarization which renders them difficult of esterification. Nitrocellulose, loose or in the form of collodion, decreases considerably in viscosity and the alcohol solubility increases. This is true, however, of only high-viscosity nitrocellulose. Samples with very low viscosities are unaffected by ultraviolet light. Traces of phenolic compounds produce intense yellow coloration with nitrocellulose products exposed to ultraviolet. The viscosity of acetone-soluble nitrocellulose also decreases on exposure but the degree of acetylation is unaffected. Films of cellulose acetate containing phenolic compounds become colored when irradiated. The irradiation of benzyl cellulose, in powder form, results in the formation of a high content of insoluble matter; irradiation of a benzyl cellulose solution does not decrease its viscosity. Other celluloses remain stable when irradiated; the viscosity of ethyl cellulose Celloidin is considerably reduced by irradiation. (See further Chapter 30.)

Long exposure of mercury fulminate, $Hg(ONC)_2$, to ultraviolet converts it to a black, more flammable but less explosive compound of equal mercury content.[210]

Sulfur Compounds

Carbon disulfide in admixture with argon undergoes a partial decomposition when exposed to bright sunlight and the sides of the containing vessel become coated with a brown deposit;[211] when exposed to diffused light, it remains unaltered. Bruhat and Pauthenier[212] have observed the decomposition of carbon disulfide by ultraviolet rays. When this substance is exposed in quartz cells to the quartz mercury arc, a deposit of sulfur is formed on the walls. In order to fix the sulfur, the interior of the cells was coated with a thin film of silver, which is transparent to the ultraviolet. For a six-hour exposure, the long wave-length limit of decomposition was found to be at 3660A.

Light catalyzes a reaction of mercaptan in contact with copper and with mercury in the presence of air.[213] When aqueous neutral solutions or alkaline solutions of sodium hydrosulphide, ethyl mercaptan, thioglycollic acid, cysteine, etc., are exposed to the radiation of a strong mercury arc, hydrogen is produced with the simultaneous formation of the corresponding disulfide compound. The quantum efficiency with respect to hydrogen formation is always much less than one, indicating that reverse reactions occur. The primary process is probably a decomposition into RS and H. In aqueous solution, where a certain amount of the anion RS′ is present the process may be $RS'(HOH)+h\nu \rightarrow RS+H+OH'$. This is followed by the formation of hydrogen from hydrogen atoms and of RSSR from two RS. A splitting of the RSH compound into RH and S may also occur as the primary process.

Many sulfhydryl compounds react with fluorescent dyestuffs in the dark. Irradiation with light absorbed by the dyestuff accelerates this reaction.[214]

Rathke[215] showed that the photopolymerization product of thiophosgene is a

[209] Clément, L., Rivière, C., and Beck, A., *Chimie et industrie*, Special No. 702 (March, 1932); *Chem. Abs.*, **26**, 3662 (1932).
[210] Patry, M., and Laffitte, P., *Bull. soc. chim.*, **51**, 1205 (1932).
[211] Berthelot, D., *Ann. Chim. Phys.*, **19**, 150 (1900).
[212] Bruhat, G., and Pauthenier, M., *Compt. rend.*, **178**, 1536 (1924).
[213] Dittrich, E., *Brennstoff-Chem.*, **15**, 148 1934); *Chem. Abs.*, **28**, 5806 (1934).
[214] Weiss, J., and Fishgold. H., *Nature*, **137**, 71 (1936).
[215] Rathke, B., *Ber.*, **21**, 2539 (1888).

dimer. Schönberg and Stephenson [216] confirm this, but believe it to be 2,2,4,4-tetrachloro-1,3-dithiacyclobutane, $Cl_2C<\begin{matrix}S\\C\end{matrix}>CCl_2$ rather than $ClCS_2CCl_3$, and that its condensation product with aniline is 4,4-dichlor-1,3-dithiacyclobutane-2-one anil. It turns brown when illuminated a short time and is depolymerized to thiophosgene in petroleum ether by the light of a quartz lamp.

Lifschitz and Froentjes [217] prepare the β-form of ethyl-α-thiolactic acid platinum, $Pt(CH_3CHSC_2H_5COO)_2$, from the α-form by exposure to the quartz mercury lamp, or better by exposure in aqueous solution to direct sunlight.

Organometallic Compounds

Lead tetramethyl and tetraphenyl decompose in ultraviolet light, which is absorbed continuously, into metallic lead and hydrocarbons. The former yields methyl radicals. For the vapor phase reaction, the quantum yield is 1.11, but in trimethylpentane, it is about 0.39, as determined by a method employing radioactive indicators. In the vapor phase reaction, oxygen breaks the chains.[218] The absorption spectrum of dimethyl zinc shows a continuum at approximately 2400A, that of diethyl zinc shows diffuse bands with an overlapping continuum at approximately 2400A, and lead tetraethyl shows a quite sharp band in the region between 2300 and 2700A.[219]

Mercury dimethyl, irradiated by the 2537A line, yields mercury, methane and ethane with a quantum yield of unity. Ethane constitutes 93 per cent of the hydrocarbons.[220] Methane is formed in amounts increasing at increasing temperatures. The primary process may yield mercury and ethane directly, although subsidiary processes may give free methyl radicals. At 462°K the quantum yield rises to 2.21, chains being involved. At room temperature in the presence of nitric oxide, a white solid is formed, but the quantum yield for the disappearance of mercury dimethyl is still unity. Aerosols [221] have been prepared by the photochemical decomposition of mercury dimethyl.

Space does not permit the discussion of the interesting chemiluminescence of the Grignard compounds, nor of their photovoltaic effects.[222]

Little work has been reported on the effects of irradiating such compounds. Gilman and Heck [223] note that although either heat or ultraviolet irradiation transforms isobutyl bromide to tertiary butyl bromide reversibly, irradiation produces no effect on isobutyl magnesium bromide or tertiary butylmagnesium chloride.

Müller, Frankenburger and Grassner [224] remove metal carbonyls from synthetic methanol or other liquids containing less than 10 per cent of iron or other metal carbonyl by exposure to ultraviolet rays, which also act on any aldehydes or ketones present. According to Reihlen, Gruhl and von Hessling [225] irradiation

[216] Schönberg, A., and Stephenson, A., *Ber.*, **66B**, 567 (1933).

[217] Lifschitz, I., and Froentjes, W., *Z. anorg. Chem.*, **224**, 173 (1935).

[218] Leighton, P. A., and Mortensen, R. A., *J. Am. Chem. Soc.*, **58**, 448 (1936).

[219] Thompson, H. W., *J. Chem. Soc.*, 790 (1934); *Proc. Roy. Soc.*, **150A**, 603 (1934); see also Thompson, H. W., and Frewing, J. J., *Nature*, **135**, 507 (1935).

[220] Linnett, J. W., and Thompson, H. W., *Trans. Faraday Soc.*, **33**, 501, 874 (1937); see also Prileshaeva, N., and Terenin, A., *Ibid.*, **31**, 1483 (1935); *Acta Physicochim. U.R.S.S.*, **1**, 759 (1934); *Chem. Abs.*, **29**, 7798 (1935); Cunningham, J. P., and Taylor, H. S., *J. Chem. Phys.*, **6**, 359 (1938).

[221] Harms, J., and Jander, G., *Kolloid-Z.*, **77**, 267 (1936).

[222] Dufford, R. T., *J. Phys. Chem.*, **35**, 988 (1931); **37**, 709 (1933).

[223] Gilman, H., and Heck, L. L., *Bull. soc. chim.*, **45**, 1095 (1929).

[224] Müller, C., Frankenburger, W., and Grassner, F., U. S. P. 1,679,256, July 31, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **28**, 3669 (1928).

[225] Reihlen, H., Gruhl, A., and von Hessling, G., Annalen, **472**, 268 (1929); *Brit. Chem. Abs.*, **1929A**, 1050.

of a mixture of ethyl mercaptan and an excess of iron pentacarbonyl greatly accelerates the reaction by which are formed hydrogen, carbon monoxide and *bis*-ironmercaptotricarbonyl:

$$2Fe(CO)_5 + 2C_2H_5SH \longrightarrow 4CO + H_2 + Fe_2(SC_2H_5)_2(C_3O_3)_2$$

A secondary reaction also occurs in which there is probably a slow decomposition of the *bis*-ironmercaptotricarbonyl to iron mercaptide.

With a mixture of equal volumes of the reactants at 3° to 5°C., the ratio of hydrogen to carbon monoxide evolved is 1:9.2. This is due to the reaction yielding instead of 4 molecules of carbon monoxide and one of hydrogen, three of carbon monoxide and one of formaldehyde, which is polymerized during the irradiation. In both of these cases, the primary reaction seems to be the loss of one molecule of carbon monoxide from two molecules of iron pentacarbonyl with the formation of $Fe_2(CO)_9$, which then reacts with two molecules of the mercaptan to yield the *bis*-ironmercaptotricarbonyl and $H_2C_3O_3$. This latter product then breaks down to yield three molecules of carbon monoxide and one of hydrogen at the higher temperatures, or two molecules of carbon monoxide and formaldehyde at low temperatures.

When a mixture of one volume of iron pentacarbonyl and five of acetylacetone is irradiated at about 30° until evolution of gas ceases, the products formed are hydrogen, carbon monoxide, ferric acetylacetone and a substance which is probably an impure peroxide of ferrous acetylacetone. From 20 to 25 per cent of the carbonyl is unchanged. Nickel carbonyl and acetyl chloride react at 50° to 55°C., but the reaction is not affected by irradiation.

The decomposition of iron pentacarbonyl in toluene and alcohol may be sensitized by pinacyanol to wave-lengths longer than 6400A.[226]

[226] Fedorov, F. P., and Talmud, D. L., *J. Phys. Chem. (U.S.S.R.)*, **8**, 789 (1936); *Chem. Abs.*, **31**, 1702 (1937).

Chapter 25

Aromatic Compounds

Berthelot and Gaudechon [1] called attention to the stability of a number of typical aromatic compounds toward ultraviolet radiations. This is in general agreement with the stability of the aromatic nucleus toward heat and chemical reagents. A similar stability has also been noted in other cyclic compounds, such as pyrrole, furfural, pyridine and a few alkaloids. In substituents which may be present, however, may occur any of the types of photochemical change encountered in these substances when unattached to the benzene ring. When the double linkings in the ring have been saturated, as in hexahydrobenzene and piperidine, ultraviolet irradiation may cause decomposition. Cyclopropane, which does not absorb wave-lengths longer than 2000A, undergoes a mercury-sensitized photopolymerization under the influence of the 2537A line to a colorless oil of high boiling point.[2]

Hydrocarbons

Berthelot [3] found that benzene remains unaltered when exposed to bright sunlight for several months in sealed tubes containing hydrogen or argon, although it combined with oxygen, yielding resinous products, if placed over mercury. A brown sediment, derived from the thiophene present in the benzene, formed at the junction of the liquids.[4]

Benzene vapor exhibits a complex absorption spectrum, analyses of which have been given by Henri.[5] The absorption of light produces only excited states, and most is reëmitted as fluorescence. From the fluorescence spectrum, Almasy[6] has drawn certain conclusions as to a predissociation of the molecule. Actually, however, little decomposition can be effected below about 600°C. by irradiation. With increasing temperatures, the fine structure of at least four of the bands of the benzene vapor spectrum successively disappears, and underlying continuous absorption increases. Henri and Cartwright suggested that incompletely separated molecules of C_3H_3 are formed by an excessive folding of the benzene ring, but that these recombine on cooling. This was proposed in an attempt to account for the predissociation spectra observed at higher temperatures.

In hexane, benzene exhibits a series of about seven relatively broad bands.[7] Kwieninski and Marchlewski [8] locate the maxima of six bands at 2648, 2608, 2546,

[1] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 376 (1911).

[2] Harris, L., Ashdown, A. A., and Armstrong, R. T., *J. Am. Chem. Soc.*, **58**, 852 (1936).

[3] Berthelot, D., *Ann. Chim. Phys.*, **19**, 150 (1900).

[4] *J. Soc. Chem. Ind.*, **47**, 727 (1928); *Report of Joint Research Committee of the National Benzol Association, and the University of Leeds*, 237 (1928).

[5] Henri, V., *J. phys. Radium*, **3**, 181 (1922); Henri, V., and Cartwright, C. H., *Compt. rend.*, **200**, 1532 (1935); Kistiakowsky, G. B., and Solomon, A. K., *J. Chem. Phys.*, **5**, 609 (1937).

[6] Almasy, F., *Naturwiss.*, **20**, 296 (1932); Almasy, F., and Shapiro, C. V., *Z. physik. Chem.*, **25B**, 391 (1934); Kistiakowsky, G. B., and Nelles, M., *Phys. Rev.*, **41**, 595 (1932).

[7] Klingstedt, F. W., *Compt. rend.*, **175**, 1065 (1922); see also Orndorff, W. R., Gibbs, R. C., McNulty, S. A., and Shapiro, C. V., *J. Am. Chem. Soc.*, **50**, 831 (1928); Shapiro, C. V., and Gibbs, R. C., *Phys. Rev.*, **31**, 310 (1928).

[8] Kwieninski, L., and Marchlewski, L., *Bull. Acad. Polonaise*, **A**, 255 (1929); *Chem. Abs.*, **24**, 783 (1930).

2490, 2433 and 2390A. The spectrum is of importance because it frequently appears in the absorption spectra of other not especially purified compounds of which benzene is a contaminant. As such, it has been erroneously reported as the absorption spectrum of substances, such as ether, contaminated by it. Indeed, the presence of small amounts of benzene vapor in the atmosphere can be detected and the benzene determined by drawing the air through alcohol and then taking the absorption spectrum. As little as 0.1 mg. per liter of air can be determined with an accuracy of about 5 per cent (in the absence of homologs) in a one liter sample.[9]

The absorption of the homologs of benzene has also been extensively studied.[10] In general, the addition of alkyl groups into benzene leads to a fusion, more or less complete, of the benzene bands.

Kailan [11] compared the action of radium and of ultraviolet rays upon toluene. The former changed less than 0.25 per cent of a sample of toluene exposed for two years. The products formed included benzaldehyde, benzoic acid, and apparently, formic acid. The principal product consisted, not of benzoic acid, but of a yellow, viscous mass composed presumably of hydrocarbons and of condensation products of benzaldehyde. Changes of a similar nature and order of magnitude were said to have been produced by 22 hours of exposure to the radiation from a quartz mercury lamp at a distance of 8 to 9 centimeters. In the presence of water, the action was slightly increased and some oxalic acid was also formed.

The fact that the most easily isolable products of the autoxidation in light of benzene homologs are carboxy-acids was attributed by Suida [12] to the relative stability of intermediate products. He believed that, with the quartz lamp as source, the velocity of the first stage of the oxidation could be approximately measured by the amount of peroxide formation, estimated by the liberation of iodine from acidified potassium iodide. The amount of carboxylic acid formed could not, however, be entirely due to the decomposition of peroxide. More recent workers have contributed to this work, but an understanding of the mechanism of the process is not complete.

The oxidation of xylene occurs more than twice as rapidly as that of toluene, para-xylene oxidizing more rapidly than the ortho isomer. The process is accelerated by the addition of small quantities of nitrobenzene, or of one of the nitrotoluenes.

According to Sudborough, Watson and Narayanan [13] it was claimed by Eckert [14] that 40 per cent yields of benzoic acid could be obtained in six weeks from toluene by atmospheric oxidation in sunlight in the presence of anthraquinone. In a repetition and extension of these experiments, Sudborough and co-workers used 200-cc. quartz flasks containing 50 gm. of toluene and 5 gm. of anthraquinone. The flasks were filled with oxygen and connected with a reservoir of that gas.

[9] Laurian, P., *14me Congr. chim. ind. Paris*, Oct. 1934, 6 pp.; *Chem. Abs.*, **29**, 6173 (1935). For data on the absorption of solid benzene, see Pringsheim, P., *Physik. Z.*, **27**, 856 (1926). Kronenberger, A., and Pringsheim, P., *Z. Physik*, **40**, 75 (1926). For the Schumann region, see Price, W. C., and Wood, R. W., *J. Chem. Physics*, **3**, 439 (1935).

[10] Pestemer, M., and Gübitz, O., *Monatsh.*, **64**, 426 (1934); Henri, V., and Walter E., *Compt. rend.*, **176**, 746 (1923); Conrad-Billroth, H., *Z. physik. Chem.*, **B29**, 170 (1935); Wolf, K. L., and Herold, W., *Z. physik. Chem.*, **B13**, 210 (1931); **B21**, 389 (1933); Radulescu, D., and Dragulescu, C., *Physik. Z.*, **36**, 66 (1935). Aubert, M., and Gheorghiu, T., *Ann. combustibles liquides*, **8**, 451 (1933); *Chem. Abs.*, **29**, 2448 (1935). Ramart-Lucas, Mme., and Amagat, P., *Compt. rend.*, **188**, 638 (1929); *Bull. soc. chim.*, **51**, 108 (1932); Horio, M., *J. Soc. Chem. Ind. Japan*, **37**, 135 (1934).

[11] Kailan, A., *Monatsh.*, **40**, 445 (1920); *J. Chem. Soc.*, **118**, i, 538 (1920).

[12] Suida, H., *Monatsh.*, **33**, 1255 (1912).

[13] Sudborough, J. J., Watson, H. E., and Narayanan, B., *J. Indian Inst. Sci.*, **8A**, 1 (1925); British P. 182,487; *J. Soc. Chem. Ind.*, 782 (B.1925); John, H., *Ber.*, **58B**, 1563 (1925).

[14] Eckert, A., Indian P. 8425; *Ber.*, **58B**, 313 (1925).

They were rocked at such a rate that the liquid was continuously splashed over the upper part of the interior surface exposed to the light. The temperature was 63-6°C. when the source was a mercury arc and 29-50°C. when sunlight was employed. The amount of acid determined by titration always exceeded that which could be isolated as benzoic acid, probably because of the formation of some formic acid. The amount of acid formed was roughly proportional to the time of exposure and was markedly dependent upon the amount of water present. The yield of acid in sunlight ranged from 0.76 per cent with 2.5 gm. water and 2.03 per cent with 25 gm. of water after 60 hours to 6.60 and 17.3 per cent, respectively, after 400 hours. In ultraviolet light, the values were: after 200 hours, 4.7 per cent with 2.5 gm. water and 15.7 per cent with 25 gm. water and, after 600 hours, 16.3 and 34.7 per cent. The addition of nitrobenzene as catalyst had practically no effect. The presence of oxygen was essential. Meta-xylene and mesitylene showed no marked oxidation after 200 hours of ultraviolet treatment. It was found by Castiglioni[15] that one and a half times as much benzoic acid was formed in a given time when Uviol flasks were used as when ordinary glass flasks were employed.

The discrepancy between the reports regarding the effect of nitrobenzene may have been due to a slow photoreaction between toluene and nitrobenzene which occurs even under nitrogen and in the absence of anthraquinone. Vecchiotti and Zanetti[16] find that a large quantity of nitrobenzene (100 gm.) and 20 gm. of toluene give, after six months in sunlight, 20 gm. of benzoic acid and *p*-aminophenol. This indicates that the side-chain of the toluene is oxidized and that the nitrobenzene is reduced to aminophenol. This reaction had been observed previously by Ciamician and Silber.[17]

Subsequent observations of the anthraquinone-sensitized oxidation of toluene by Kothari and Watson[18] indicated the rate to be greatest in the presence of 1 per cent of catalyst. The rate is initially slow, but gradually speeds up and eventually becomes constant. They believed the fraction of toluene oxidized, 8.3 to 9.8 per cent, to be larger in proportion to time when the sun was the source than when the mercury arc was employed. Uranium salts had irregular effects as catalysts.[19]

Xylene mixed with an aromatic nitro-hydrocarbon is reported to contain more active oxygen after exposure to light and oxygen than pure xylene exposed to light and oxygen, but Suida[20] found that the presence of a nitro- compound reduced the total yield of oxidation product, although considerable quantities of toluic aldehyde were present. Thus in the presence of a nitro-hydrocarbon the less stable products of oxidation (aldehydes and peroxides) remained, while the pure chemical reaction (the decomposition of these primary products to the next higher and more stable stage of oxidation) was delayed. It was possible by cooling in carbon dioxide and ether to bring almost to a standstill the decomposition of the benzene hydroperoxide (formed from benzaldehyde by the action of ultraviolet). The product of the primary autoxidation process could not be isolated, as it decomposed into benzoic acid within a few minutes after removing it from

[15] Castiglioni, A., *Gazz. chim. ital.*, **63,** 818 (1933); *Brit. Chem. Abs.*, **A,** 264 (1934); see, however, John, H., *Ber.*, **58B,** 1563 (1925); *Chem. Abs.*, **20,** 337 (1926).

[16] Vecchiotti, L., and Zanetti, G., *Gazz. chim. ital.*, **60,** 479 (1930); *Chem. Abs.*, **25,** 251 (1931).

[17] Ciamician, G., and Silber, P., *Gazz. chim. ital.*, **33,** 354 (1903); **36,** 174, 176, 190, 197 (1906).

[18] Kothari, C. J., and Watson, H. E., *J. Indian Inst. Sci.*, **A14,** 11 (1931); *Chem. Abs.*, **26,** 378 (1932).

[19] See also Nozicka, F., U. S. P. 1,945,067, Jan. 30, 1934; *Chem. Abs.*, **28,** 2273 (1934); German Patent 624,964; *Chem. Abs.*, **30,** 4870 (1936); and Kreidl, I., U. S. P. 1,971,042, Aug. 21, 1934, for other catalysts related to anthracene or anthraquinone.

[20] Suida, H., *Ber.*, **47,** 467 (1914); *Monatsh. Chem.*, **33,** 1268 (1912).

the cooling mixture. Little is known as yet regarding the mechanisms of these oxidations.

Plotnikow[21] notes that sunlight acts on solutions of potassium dichromate containing various organic compounds. Triphenylmethane is unaltered and benzene remains almost unchanged even in the presence of ferric chloride, but toluene yields a variety of products. Phenol forms benzoquinone and a mixture of polyhydric phenols. Ortho- and meta-xylenes yield tolualdehydes and acids, and some formic acid is formed from *p*-xylene. Quinol forms primarily benzoquinone, but phthalic acid also has been isolated from the reaction products. Resorcinol and pyrocatechol yield trihydric phenols, benzoquinone and similar compounds. A solution containing *o*-cresol decomposes with evolution of carbon dioxide and separates into two layers, of which the lower contains unchanged cresol, chromic hydroxide, and a tarry substance, and the upper, benzoic and oxalic acids. Naphthalene and α-naphthol are unchanged after ten months of irradiation. Some aniline dyes give fluorescent solutions. Aniline is converted rapidly into aniline black, and *p*-aminophenol into benzoquinone and ammonia. Results with pseudocumene indicate that the possibility of terpene formation is dependent on a symmetrical molecular structure. Dihydroxyanthraquinone breaks down into benzoquinone and carbon dioxide. Mixtures of isopulegol and ammonium dichromate in various proportions yield on irradiation in aqueous or alcohol solutions only about 1 per cent of isopulegone, whereas isoeugenol undergoes extensive oxidation.

Substitution Products of Benzene. Although the absorption spectra of the various halogen substitution products of benzene and its homologs have been recorded and in some cases analyzed,[22] little is known regarding their photochemical decompositions or reactions.

Without catalysts, *p*-bromobenzenesulfonate undergoes no decomposition in darkness and less than 2 per cent in light.[23] In the presence of charcoal, 0.65 to 0.95 per cent decomposition occurred in darkness and 2.28 to 3.21 per cent in the light of a carbon arc. The corresponding values in the presence of copper were 3.78-5.26 and 5.83-7.79 per cent. In the presence of both copper and charcoal, the values were 10.71 to 23.70 per cent decomposed in darkness and 14.29 to 26.28 per cent in light.

Photochemical Nitrations and Nitro- Compounds

In the photochemical reaction in sunlight between benzene and a mixture of nitric and sulfuric acids, Sollazzo[24] finds that there are successively formed nitrobenzene, nitrosobenzene, azoxybenzene and finally the salts of azoxybenzenesulfonic acid.

Bass and Johnson[25] allowed nitrogen peroxide to react with benzene for three months in sealed tubes both in darkness and in sunlight. The only nitration products identified were the mono- and di-nitroderivatives, formed in very small yield. Anhydrous nitrogen peroxide gas was passed over 50 gm. of dry toluene in a water-cooled quartz tube exposed to a quartz mercury arc for six hours. In addition to 2.5 gm. of benzoic acid and 32.0 gm. of toluene, there was obtained 13.0 gm. of an unstable low-boiling (40-80°C.) liquid which showed no definite boiling point, but decomposed into toluene and nitrogen peroxide. They believed the nitrogen peroxide to act solely as an oxidizing agent, practically no nitration taking place.

[21] Plotnikow, J., *Chem. Ztg.*, **52,** 669 (1928); *Chem. Abs.*, **22,** 4380 (1928).

[22] Errera, J., and Henri, V., *J. Phys. Radium*, **9,** 205, 249 (1928); Conrad-Billroth, H., *Z. physik. Chem.*, **B19,** 76 (1932); **B25,** 139, 217 (1934); Klingstedt, F. W., *Z. physik Chem.*, **20B,** 125 (1933).

[23] Sandonnini, C., *Atti R. Accad. Lincei*, **2,** 427 (1925); *Chem. Abs.*, **20,** 1018 (1926).

[24] Sollazzo, G., *Officina*, **4,** 268 (1931); *Chem. Abs.*, **26,** 1862 (1932).

[25] Bass, L. W., and Johnson, T. B., *J. Am. Chem. Soc.*, **46,** 456 (1924).

More recently, however, it was found[26] that when 40 gm. of toluene were passed in vapor form with 180 to 200 gm. of nitrogen peroxide and 45 to 50 liters of carbon dioxide at 14° to 15°C. during two hours before or through a jacketed quartz mercury-vapor lamp, 55 per cent of the toluene reacted, giving about 5 gm. of the side-chain nitration product, and 27-28 gm. of a mixture of mononitrotoluenes. No dinitrotoluene and no benzoic acid were produced. Raising the temperature to 58-60°C. did not affect the side-chain nitration, but lowered the yield of the nitrotoluenes to 15 gm. In the absence of radiation, less toluene reacted, but the relative amounts of side-chain and nuclear substitution were but little affected. The nitration of benzene was but little affected by irradiation. Titov and Baryshnikova[27] obtained rather similar results under conditions, such as low concentration and illumination, which favored the dissociation of the N_2O_4. They did observe a considerable amount of disubstitution in the side chain, as well as some benzaldehyde and benzoic acid formation. These products were secured in the absence of illumination. In sunlight or the light of the mercury arc, all the reactions were accelerated except that the ring substitution was reduced approximately 4 to 9 per cent.

Irradiation has little effect on the nitration of benzene, *n*-hexane or cyclohexane. In general, it is helpful only when the completely symmetrical structure of the benzene molecule is disturbed by the presence of a side-chain.[28]

To obtain information regarding the photochemical action of nitrobenzene on various organic compounds, a field already investigated by Ciamician and Silber,[29] Vecchiotti and Zanetti [30] exposed it in an atmosphere of nitrogen to sunlight for six months in contact with the substance to be tested. In the reaction with cinnamic acid, the products obtained included benzoic acid, carbon dioxide, benzanilide, azoxybenzene and hydroxyazobenzene. It was assumed that the double bond of the cinnamic acid was ruptured, with the formation of benzaldehyde and OHCCOOH, these products being oxidized to benzoic and oxalic acids. On further oxidation, cinnamic acid yields carbon dioxide. The nitrobenzene is reduced to nitrosobenzene. The formation of the remaining three compounds is accounted for by reference to the explanation given by Ciamician and Silber [31] for the action of nitrobenzene on benzaldehyde. Benzanilide may be formed from benzaldehyde by either of the reactions:

$$C_6H_5NO_2 + 3C_6H_5CHO \longrightarrow C_6H_5NHCOC_6H_5 + 2C_6H_5COOH.$$
$$C_6H_5NO + 2C_6H_5CHO \longrightarrow C_6H_5NHCOC_6H_5 + C_6H_5COOH.$$

Azoxybenzene may be formed by

$$2C_6H_5NO + C_6H_5CHO \longrightarrow C_6H_5N(:O):NC_6H_5 + C_6H_5COOH.$$

or by analogy with the Bamberger [31a] reaction of nitrosobenzene and C_6H_5HNOH by

$$C_6H_5NO + C_6H_5(HO)NCOC_6H_5 \longrightarrow C_6H_5N(:O):NC_6H_5 + C_6H_5COOH.$$

[26] Schorigin, P., and Toptschiev, A., *Ber.*, **67**, 1362 (1934); *J. Gen. Chem. Russ.*, **5**, 549 (1935); *Brit. Chem. Abs.*, **A**, 61 (1936).

[27] Titov, A. I., and Baryshnikova, A. N., *J. Gen. Chem. U.S.S.R.*, **6**, 1801 (1936); *Chem. Abs.*, **31**, 4285 (1937).

[28] Schorigin, P., and Toptschiev, A., *loc. cit.*; for attempts at substitution of hydrocarbons by NOCl during irradiation, see Perrot, R., *Compt. rend.*, **198**, 1424 (1934).

[29] Ciamician, G., and Silber, P., *Gazz. chim. ital.*, **33**, 354 (1903); **36**, 174, 176, 190, 197 (1906).

[30] Vecchiotti, L., and Zanetti, G., *Gazz. chim. ital.*, **60**, 479 (1930); *Chem. Abs.*, **25**, 251 (1931).

[31] Ciamician, G., and Silber, P., *Compt. rend. Acad. Lincei*, **14**, 265 (1905).

[31a] *Ber.*, **35**, 1606 (1902).

The last of the three compounds may be formed from $C_6H_5N(:O):NC_6H_5$ by transposition.[32]

$$C_6H_5\cdot\underset{\underset{O}{\|}}{N}=N\cdot C_6H_5 \longrightarrow C_6H_5N=N\cdot C_6H_4OH$$

or by

$$C_6H_5NO + C_6H_4(OH)NH\cdot COC_6H_5 \longrightarrow HO\cdot C_6H_4N=NC_6H_5 + C_6H_5COOH$$

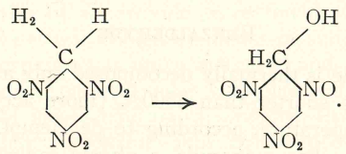
Even in darkness, cinnamic acid and nitrobenzene gave benzoic acid and azoxybenzene.

In the photochemical reaction of nitrobenzene and naphthalene, a trace of *β*-naphthol was the only product identified.

On exposure to sunlight, Sollazzo [33] found a mixture of ethanol, ammonium hydroxide and *m*-dinitrobenzene to become red-yellow. In the case of amyl alcohol, the color was cherry-red; it was permanent in darkness.

Illumination of 1-styryl-3-bromostyryl-4, 6-dinitrobenzene gives 2-phenyl-5-styryl-6-nitroisatogen.[34]

Molinari and Giua are said [35] to have observed 2,4,6-trinitrotoluene to turn slowly brown on the surface when exposed to bright daylight. The melting point dropped from 80° to 74° in three months. Custis [36] found that a more rapid reaction occurs when the material was exposed to an iron arc, but a mercury arc did not prove effective. Schultz and Ganguly [37] attribute the red coloration observed after the prolonged action of light on 2,4,6-trinitrotoluene in the presence of oxygen, hydrogen, nitrogen or *in vacuo,* to the production of two tautomeric quinonoximes, $C_7H_5O_6N_3$, of melting points above 280°C. They can be separated by their differing solubilities in cold acetone. Each dyes wool red. They are considered to be 2-nitro-6-nitroso-5-hydroxymethyl-*p*-benzoquinone-4-oxime and 2-nitro-4-nitroso-5-hydroxymethyl-*o*-benzoquinone-2-oxime. The course may involve the migration of an oxygen atom from a nitro- group to the methyl group, as in



In acetone solution, the process may stop here, the product melting at 108-111°C. In the case of the solid, a repetition of the process yields the unstable 4-nitro-2,6-dinitrosodihydroxymethylbenzene. One hydroxyl migrates to the nucleus, and then passes its hydrogen to one or the other nitroso- group, forming the *o*- and *p*-oximes. The assumption that only the nitro- groups in the 2 and 6 positions are reduced is supported by the observation that 2,6-dinitrotoluene is converted by exposure to light into a yellow substance, probably 2,6-dinitroso-4-hydroxybenzyl

[32] Knipscheer, H. M., *Rec. trav. chim.*, **22**, 14 (1903).

[33] Sollazzo, G., *Officina*, **4**, 340 (1931); *Chem. Abs.*, **26**, 3729 (1932); *Boll. chim. farm.*, **72**, 913 (1933); *Brit. Chem. Abs.*, **A**, 264 (1934); *Chem. Abs.*, **28**, 5758 (1934).

[34] Ruggli, P., and Zimmerman, A., *Helv. Chim. Acta*, **15**, 865 (1932); *Chem. Abs.*, **27**, 292 (1933).

[35] Escales, R., "Die Explosivstoffe mit besonderen Berüchsightigung der neueren Patente." *Heft*, **6**, "Nitrosprengstoffe," p. 295. Leipzig, Vereinigg. wissensch. Verleger, 1915.

[36] Custis, H. H., *J. Frank. Inst.*, **184**, 876 (1917); *Chem. Trade J.*, **62**, 90; *Chem. Zentr.*, 208, I (1928).

[37] Schultz, G., and Ganguly, K. L., *Ber.*, **58B**, 702 (1925).

alcohol, although *p*-nitrotoluene is completely unchanged. The presence of a nitro- group in the *para* position appeared to retard the change, since 2,4-dinitrotoluene is almost stable to light. 2,4,6-Trinitrobenzyl alcohol in benzene and 2,4,6-trinitrobenzyl bromide, as a solid or in benzene, are also sensitive to light.

It was believed by Krauz and Turek[38] that exposure of trinitrotoluene in thin layers to sunlight increased its sensitiveness to shock. This was attributed to a decomposition leading to the formation of both picric and trinitrobenzoic acids. Metals or metal oxides were supposed to hasten this change, which occurred to a sufficient extent to change the melting point in four months from 81.4° to 73.5°C. These results have been critically examined by Wichart and Donat[39] and by Lodati,[40] who find the technical products completely stable in contact with metals. The latter worker states, however, that in diffused light, the compound formed some nitrous vapors in three months.[41]

According to Sachs and Hilpert,[42] the nitrobenzylidene group should be light-sensitive. This was confirmed by I. and H. Tănăsescu[43] in studies of the action of sunlight on *o*-nitrobenzylideneglycol, $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH{\cdot}C_6H_4NO_2$, which yielded a white crystalline isomer *o*-$NO{\cdot}C_6H_4{\cdot}C(OH){\cdot}O{\cdot}CH_2{\cdot}CH_2O$, melting at 128°C. to a green liquid which readily hydrolyzed on boiling with acid or base to form glycol and *o*-nitrosobenzoic acid. A similar migration of oxygen from a nitro-group to form an alcohol group (mentioned by Schultz and Ganguly in the case of trinitrotoluene) was observed in di-*o*-nitrobenzylideneerythritol. A similar type of behavior is also encountered in the case of *o*-nitrobenzaldehyde. Tănăsescu and Macovski[44] have extended this work to include the changes in 1,2,5,6-di-*o*-nitrobenzylidenedulcitol which gives a resin, possibly by partial isomerization and *p*-nitrobenzylidene-3-benzoylglycerol. Included are also the *o*-nitrobenzylidene-acetals of a number of other glucides, such as mannitol and sorbitol. The structure of the photochemical isomerization products was not definitely established, these authors believing an open-chain formula of the type $O\text{-}ROCH_2CH_2OCOC_6H_4NO$ the most adequate. Recently, the corresponding compounds of galactose, α-methyl-galactose, mannose, rhamnose, fructose, lactose and sucrose have been found to give isomerizations when irradiated in chloroform and benzene solutions.[45]

Benzaldehyde

Although benzaldehyde is thermally decomposed only at temperatures of 400°C. and higher, wave-lengths shorter than 2600A (more accurately 2438A) produce a photolysis at room temperature, according to de Hemptinne.[46] He believed the primary products to be carbon monoxide, a phenyl radical and a hydrogen atom, the latter combining to produce benzene. The energy necessary for this was calculated to be 115.7 kcal., corresponding to 2461A, at which the "total" absorption band of the benzaldehyde spectrum begins.

[38] Krauz, C., and Turek, O., *Z. ges. Schiess-u. Sprengstoffw.*, **20**, 49 (1925); *Chem. Abs.*, **19**, 2747 (1925); *Chem. Age (London)*, **13**, 392 (1925); *Chem. Abs.*, **20**, 824 (1926).

[39] Wichart and Donat, *Z. ges. Schiess-u. Sprengstoffw.*, **20**, 69 (1925).

[40] Lodati, D., *Giorn. Chim. Ind. Appl.*, **7**, 572 (1925); *Chem. Abs.*, **20**, 3815 (1926); but see also, Sucharevskii, M., *Z. ges. Schiess-u. Sprengstoffw.*, **20**, 40 (1927); *Chem. Abs.*, **21**, 3462 (1927).

[41] For spectrographic studies of this reaction, see also Pavlik, M., *Chimie et Industrie, Special No.*, 245 (June, 1933).

[42] Sachs, F., and Hilpert, S., *Ber.*, **37**, 3425 (1904).

[43] Tănăsescu, I., and Tănăsescu, H., *Bul. soc. stiinte Cluj*, **2**, 369 (1925); *Chem. Abs.*, **20**, 749 (1926).

[44] Tănăsescu, I., and Macovski, E., *Bull. soc. chim.*, **53**, 1097 (1933); *Chem. Abs.*, **28**, 1330 (1934); *Bull. soc. chim.*, **51**, 1371 (1932); *Chem. Abs.*, **27**, 1874 (1933); *Bull. soc. chim.*, **51**, 1556 (1932); *Chem. Abs.*, **27**, 2142 (1933); *Bull. soc. chim.*, **45**, 1022 (1929); *Chem. Abs.*, **24**, 2118 (1930); *Bull. soc. chim.*, **47**, 86 (1930); *Chem. Abs.*, **24**, 2429 (1930); *Bull. soc. chim.*, **47**, 457 (1930); *Chem. Abs.*, **24**, 4270 (1930).

[45] Tănăsecu, I., and Craciunescu, E., *Bull. soc. chim.*, **3**, 581 (1936); Tanasescu, I., and Jonescu, M., *Bull. soc. chim.*, **3**, 1517 (1936).

[46] de Hemptinne, M., *Compt. rend.*, **186**, 1295 (1928); *Ann. Soc. Sci. Bruxelles*, **48B**, 98 (1928); *Brit. Chem. Abs.*, **A**, 409 (1929); *J. Phys. Radium*, **9**, 357 (1928).

The absorption spectrum has been studied recently by Almasy[47] who found three broad regions. From 3747 to 3163A, there were 159 measurable bands in the vapor; between 2963 and 2599A there were 51. At 2428 to 2349, there were six bands followed by continuous absorption. As the temperature is raised, the character of the spectrum is altered, the narrow bands fusing into broader ones indicating the occurrence of predissociation at longer wave-lengths, the higher the temperature. At 208°C the fine bands present at lower temperatures between 2966 and 1610A are continuous and radiations in this range produce photolysis. At 270°C radiations shorter than 3200A produce dissociation.

On exposure to ultraviolet rays, hexahydrobenzaldehyde yields carbon monoxide, cyclohexane and the dimer.[48] Phenylacetaldehyde does not evolve carbon monoxide, but is partly converted into a yellow oil and a brownish-red, viscous residue. Hydrocinnamaldehyde also is said to be practically unaffected by ultraviolet light. Hexahydrophenylacetaldehyde yielded a gas containing 88 per cent of carbon monoxide, hexahydrotoluene, and small quantities of polymerized products.[49] Hexahydro-β-phenylpropaldehyde, after ten hours' exposure to ultraviolet, gave carbon monoxide more slowly and in smaller quantity and highly polymerized products from which only a trimer of the original aldehyde, but no hexahydroethylbenzene, could be isolated.

Oxidation of Benzaldehyde. It was early claimed[50] that the autoxidation of either benzaldehyde or of pinene under the influence of rays from a Uviol lamp increased the electrical conductivity of oxygen. It had been found by Jorissen and Ringer[51] that when a mixture of one mole of benzaldehyde and two of acetic anhydride is exposed to the diffused light of an arc or a magnesium flame in an atmosphere of oxygen in a closed vessel, benzoylacetal peroxide could be obtained.

Suida[52] passed a current of oxygen through a solution of benzaldehyde in petroleum ether (cooled with ice), while irradiating it by a Heraeus quartz lamp at a distance of two centimeters. After six hours a considerable amount of benzoic acid and small quantities of a peroxide were found, which could not be readily isolated. When the vessel was cooled by means of solid carbon dioxide and ether, the formation of the peroxide was much increased and a white deposit with strong oxidizing properties and a pungent odor was obtained.

By a combination of iodometric and acidimetric titrations during the reaction, Bäckström[53] found that perbenzoic acid is the product of the photochemical reaction. The quantum efficiency is high, of the order of 10,000. The reaction can be inhibited. The perbenzoic acid subsequently reacts with benzaldehyde, forming benzoic acid by a pseudo-unimolecular thermal reaction, which shows little or no negative catalysis. This reaction is accelerated by light, but the quantum yield is less than 0.5 per cent of that of the reaction by which the perbenzoic acid is formed. The quantum yield for the total reaction, measured by the oxygen uptake, decreases during the progress of the reaction.

[47] Almasy, F., *J. chim. phys.*, **30**, 528, 713 (1933).

[48] Franke, A., and Sigmund, F., *Monatsh.*, **46**, 61 (1925); *cf.* also Wallach, O., and Isaac, E., *Annalen*, **347**, 331 (1906).

[49] Sigmund, F., *Monatsh.*, **52**, 185 (1929).

[50] Jorissen, W. P., and Vollgraff, J. A., *Chem. Weekblad*, **12**, 93 (1915); *J. Chem. Soc.*, **108** (ii), 80 (1915).

[51] Jorissen, W. P., and Ringer, W. E., *Chem. Weekblad*, **2**, 19; *Chem. Zentr.*, **76**, 817 (1905).

[52] Suida, H., *Ber.*, **47**, 471 (1914).

[53] Bäckström, H., *Med. K. Vetenskapsakad. Nobelinst.*, **6**, Nos. 15 and 16 (1927); Backström, H., and Beatty, H. A., *J. Phys. Chem.*, **35**, 2530 (1931).

According to Kothari and Watson [54] this decrease, which is found also in toluene solutions and by the use of an incandescent light source, is greater than could be accounted for by the retarding action of the benzoic acid. It was less when benzene was the solvent. Anthraquinone may serve as an accelerator of the reaction when toluene is the solvent, but is not effective in benzene. Benzoquinone is a strong inhibitor, and phenolic compounds also act in this way. According to Jorissen and Dekking,[55] the photoöxidation of benzaldehyde in the presence of iodobenzene induces oxidation of the latter compound.

Photochemical reactions between aldehydes and quinones have been the subject of a number of empirical observations.[56] Angeletti and Baldini,[57] found that after exposure to sunlight for six months an equimolar mixture of benzaldehyde and toluquinone in benzene gave benzoic acid, toluhydroquinone, a relatively small quantity of diethyl toluhydroquinone benzoate, an unidentified phenolic compound, and large quantities of resins. Light reduced the toluquinone to toluhydroquinone and oxidized the benzaldehyde to benzoic acid. The latter then esterified the two hydroxyl groups of toluhydroquinone. Cinnamaldehyde and toluquinone similarly gave cinnamic acid, toluhydroquinone and a monocinnamate of toluhydroquinone.[58] No compounds corresponding to the 2,5-dihydroxybenzophenone were reported by Klinger.[59]

It has been stated by Chattaway [60] that benzaldehydephenylhydrazone reddens slowly in diffused light. In sunlight, the change becomes very noticeable in a few minutes, reaching, in a few hours, a maximum intensity, the crystals having a brilliant scarlet color like that of azobenzene. The change could be produced also by the light of an iron arc, but the ultraviolet rays were not held responsible since the interposition of glass did not interfere with the effect. Hodgson and Handley [61] found no change in the phenylhydrazone of *p*-nitrobenzaldehyde under similar treatment.

Transformation of o-Nitrobenzaldehyde. The nature of the isomerization which occurs when this compound is irradiated either as a solid or in acetone solution is similar to that described on page 472 for the *o*-nitrobenzylidene glycols. An oxygen atom is removed from the nitro- group and transferred to the aldehyde group, forming in this case *o*-nitrosobenzoic acid. Weigert and Kummerer [62] showed that the amount of the reaction is proportional to the time of irradiation. In experiments in which the intensity was varied, they believed that their data indicated a slight deviation from the Bunsen-Roscoe law. When ultraviolet light was employed, the rate of the change was independent of the concentration, but when violet light was used the rate was at first proportional to the concentration.

In later work, the quantum yield was found [63] to be 0.5 when the wave-lengths 4360, 4050 or 3660A were used. To account for this, they developed a special theory in which the orientation of the molecules with respect to the electric vector

[54] Kothari, C. J., and Watson, H. E., *J. Indian Inst. Sci.*, **A14**, 11 (1931); *Chem. Abs.*, **26**, 378 (1932).

[55] Jorissen, W. P., and Dekking, A. C. B., *Rec. trav. chim.*, **57**, 829 (1938).

[56] Ciamician, G., and Silber, P., *Ber.*, **24**, 1430 (1891); **31**, 124 (1898); Klinger, H., *Annalen*, **249**, 137 (1888); Bargellini, G., and Monti, L., *Gazz. chim. ital.*, **60**, 474 (1930); *Chem. Abs.*, **25**, 96 (1931).

[57] Angeletti, A., and Baldini, V., *Gazz. chim. ital.*, **64**, 346 (1934); *Chem. Abs.*, **28**, 5422 (1934).

[58] Angeletti, A., *Atti accad. sci., Torino, Classe sci. fis., mat. nat.*, **70**, 326 (1935); *Chem. Abs.*, **30**, 1383 (1936); *Atti V Congr. Naz. Chim.*, **1**, 280 (1936); *Brit. Chem. Abs.*, **A** (II), 196 (1937).

[59] Klinger, H., *Annalen*, **382**, 211 (1911); *Chem. Abs.*, **5**, 3456 (1911).

[60] Chattaway, F. D., *J. Chem. Soc.*, **89**, 463 (1906).

[61] Hodgson, H. H., and Handley, F. W., *J. Chem. Soc.*, **1882 (1928)**.

[62] Weigert, F., and Kummerer, L., *Ber.*, **46**, 1207 (1913); see also Bowen, E. J., Hartley, H., Scott, W. D., and Watts, H. G., *J. Chem. Soc.*, **125**, 1218 (1924).

[63] Weigert, F., and Brodmann, L., *Trans. Faraday Soc.*, **21**, 453 (1926).

of the incident light was considered a determining factor. It was suggested that the transfer of an oxygen atom to an aldehyde group takes place only when the electric vector of the incident radiation corresponds to the line between the nitro- and aldehyde groups. It could be shown that only 50 per cent of the molecules would be so oriented as to react. Thus, for these molecules, the quantum yield would be unity, although the observed value was but 0.5. Such a theory lost its significance when it was found that many reactions in solutions have quantum yields varying in exact value, but less than unity. Furthermore, it has been found by some that Weigert's results [64] showed some variations from the 0.5 which his theory demands, as various wave-lengths were employed. This, however, has been denied by Weigert and Pruckner [65] after further observations. The value of 0.5 has been verified also by Leighton and Lucy [66] for 2,4-dinitrobenzaldehyde as well as for *o*-nitrobenzaldehyde. They found somewhat higher values in the case of 2,4,6-trinitrobenzaldehyde.[67] These, as well as other recent workers [68] reject the Weigert theory, and believe the usual explanations given for low quantum yields in liquid or solid-phase reactions to apply. Leighton and Lucy related the yield of 0.5 to the assumption that the N=O adjacent to the aldehyde group must be excited for the transformation to occur. They consider the processes of energy exchange between the two N=O linkings.

Janssen found the absorption spectrum of the vapor of this compound to be continuous, implying a primary photodecomposition. Zimmer, who noted the compound to be dichroic at 4360 and 4050A although not a mixture of two tautomers, found it to exhibit no appreciable fluorescence. He believed that the primary process produces nitrosobenzaldehyde and an oxygen atom. The latter could recombine with the other dissociation product in either of two ways—to restore the original compound or to form the nitrosobenzoic acid. The equal likelihood of these two processes would account for the quantum yield of 0.5. Küchler and Patat [69] found the quantum yield in the gas phase to be much higher than that in solution. At 90°C., it reached 0.75, but could be lowered to 0.5 by the presence of 700 mm. nitrogen. They did not accept the theory of a primary splitting off of oxygen and could find no evidence for the primary formation of oxygen atoms. Neither free oxygen nor nitric oxide was formed. They believed the simplest explanation of the quantum yields of 0.5 to be a deactivation of some type of excited molecule, regulated intramolecularly.

Various other compounds, as has already been indicated, undergo a similar type of transformation. Tănăsescu [70] believes all substances which contain the *o*-nitrobenzaldehyde grouping and which are light-sensitive contain a mobile hydrogen atom. An example of a light-insensitive compound is *o*-nitrocinnamaldehyde. In this case, according to Kögel, the aldehyde group differs in not being an oxygen-acceptor.[71] In the presence of pyrogallol as oxygen acceptor, however, the nitro- group of this aldehyde, as well as that of *o*-nitrobenzaldehyde, is light-

[64] Weigert, F., and Pruckner, F., *Z. physik. Chem. Bodenstein-Festband*, 775 (1931); Weigert, F., (1929).

[66] Leighton, P. A., and Lucy, F. A., *J. Chem. Physics*, **2**, 756, 760 (1934).

[67] See also Secareanu, S., and Lupas, I., *Bull. soc. chim.*, **3**, 1161 (1936); *Brit. Chem. Abs.*, **A**, 986 (1936).

[68] Wegscheider, R., *Monatsh.*, **52**, 68 (1929); Janssen, C., *Z. physik. Chem.*, **B18**, 241 (1932); Zimmer, K. G., *Ibid.*, **B23**, 239 (1933); Bowen, E. J., *Trans. Faraday Soc.*, **21**, 523 (1926).

[69] Küchler, L., and Patat, F., *Monatsh.*, **68**, 275 (1936); *Z. Elektrochem.*, **42**, 529 (1936).

[70] Tănăsescu, I., *Bull soc. chim.*, **39**, 1443 (1926).

[71] Kögel, J., *Z. wiss. Phot.*, **24**, 216 (1926); *Chem. Abs.*, **20**, 3646 (1926).

sensitive. In the case of nitroterephthaldehyde, the maximum quantum yield in the transformation into 2,4,1-nitrosoterephthaldehydic acid in acetone solution is 0.1 in light of the ranges 3740-3251 and 3740-3345A. With light of constant intensity, the rate of reaction diminishes as exposure continues. It increases with increasing light intensity, approaching a limit. Kögel assumes that before exposure the normal molecules of the aldehyde are in equilibrium in solution with an intermediate substance, and that it is this substance which reacts photochemically with the normal molecules. This conclusion, which he applies also to *o*-nitrobenzaldehyde, was based upon an observed diminution of the absorption coefficients of the solution with rise in temperature. This was ascribed to the formation of a substance with relatively small absorption coefficients.

Davies [72] notes that 5-nitro-2-methoxy-3-ethoxybenzaldehyde undergoes no change of color or melting point when exposed in pure acetone solution for 25 hours to ultraviolet rays. On the other hand, another nitration product (melting point 85°C.) of 2-methoxy-3-ethoxysalicylaldehyde obtained by precipitation with water rapidly becomes greenish-blue under the same conditions.

Aromatic Ketones

Ciamician and Silber [73] showed that when an alcoholic solution of benzophenone is exposed to sunlight, the ketone is reduced to benzopinacol and the alcohol is oxidized to aldehyde. Cohen [74] extended the observations to include a number of substituted ketones and a variety of primary and secondary alcohols. Böeseken, Cohen and Langedijk [75] gave data on the absorption of benzophenone, fluorenone and terephthalophenone for the region 3600 to 4500A and pointed out that their maximum absorption did not occur in the wave-length region which was photochemically active.[76]

To throw light on the nature of the primary reaction involved, Böeseken and Visser [77] determined the photoelectric threshold of benzophenone and found it to lie between 3025 and 2537A. The absorption band at 2600A would seem, therefore, to correspond to ionization of the molecule, a process unusually encountered in photochemical processes. No absorption bands were found in the region of excitation, 4070 to 3800A.

Having shown that a small amount of sodium alcoholate can effect the decomposition of a large amount of benzopinacol into a mixture of benzohydrol and benzophenone, Bachmann [78] combined this reaction with the photochemical reaction by conducting the latter in solutions containing a small amount of sodium alcoholate. The ketone regenerated in the decomposition of the pinacol into hydrol and ketone goes through the photochemical change again, and the series of reactions is repeated until eventually the hydrol is the sole product. In the case of benzophenone and isopropyl alcohol, the reactions are:

[72] Davies, W., *J. Chem. Soc.*, **123**, 1590 (1923).

[73] Ciamician, G., and Silber, P., *Ber.*, **33**, 2911 (1900).

[74] Cohen, W. D., *Rec. trav. chim.*, **39**, 242 (1920).

[75] Böeseken, J., Cohen, W. D., and Langedijk, S. L., *Rec. trav. chim.*, **44**, 173 (1925); **46**, 383 (1927).

[76] For more recent data on the absorption of benzophenone and other ketones, see Tasaki, T., *Acta Phytochim.*, **2**, 49, 199 (1925); **3**, 259 (1927); Anderson, L. C., *J. Am. Chem. Soc.*, **55**, 2094 (1933); Anderson, L. C., and Gooding, C. M., *J. Am. Chem. Soc.*, **57**, 999 (1935); Purvis, J. E., *J. Chem. Soc.*, **127**, 9 (1925); Rupe, H., Collin, A., and Schmiderer, L., *Helv. Chim. Acta*, **14**, 1340 (1931); Rupe, H., Pedrini, F., and Collin, A., *Helv. Chim. Acta*, **15**, 1321 (1932); Rupe, H., Collin, A., and Sigg, W., *Helv. Chim. Acta*, **14**, 1355 (1931); Ley, H., and Wingchen, H., *Ber.*, **67B**, 510 (1934).

[77] Böeseken, J., and Visser, G. H., *Rec. trav. chim.*, **47**, 1037 (1928); *Chem. Abs.*, **23**, 2660 (1929).

[78] Bachmann, W. E., *J. Am. Chem. Soc.*, **55**, 355, 391 (1933).

$$2(C_6H_5)_2CO + (CH_3)_2CHOH \longrightarrow (CH_3)_2CO + (C_6H_5)_2-\underset{\displaystyle (C_6H_5)_2-C-OH}{\overset{\displaystyle |}{C}}-OH$$

$$\underset{\displaystyle (C_6H_5)_2-C-OH}{\overset{\displaystyle (C_6H_5)_2-C-OH}{\overset{\displaystyle |}{\overset{\displaystyle |}{}}}} \xrightarrow{(CH_3)_2CHONa} \underset{\displaystyle (C_6H_5)_2-C-ONa}{\overset{\displaystyle (C_6H_5)_2C-ONa}{\overset{\displaystyle |}{\overset{\displaystyle |}{}}}} \rightleftharpoons 2(C_6H_5)_2CONa$$

$$2(C_6H_5)_2CONa + 2(CH_3)_2CHOH \longrightarrow 2(C_6H_5)_2-COH + 2(CH_3)_2CHONa$$

$$\downarrow$$

$$(C_6H_5)_2CO + (C_6H_5)_2CHOH.$$

A solution of benzophenone in isopropyl alcohol containing sodium isopropylate becomes greenish-blue on exposure to sunlight, the color being characteristic of the sodium ketyl radical. When the solution is protected from light, the color disappears by the action of the sodium ketyl radical with isopropyl alcohol. Renewed exposure to sunlight restores the color, but when after several days of exposure all of the ketone has been reduced, the solution has again become colorless.

In agreement with the observation of Cohen that Michler's ketone, phenyl-α-naphthyl ketone, fluorenone and 4-phenylbenzophenone are not photochemically reduced to pinacols, Bachmann found that Michler's ketone and phenyl-α-naphthyl ketone could not be reduced to hydrols in this way. Fluorenone underwent a different type of reaction, not photochemical. 4-Phenylbenzophenone, however, was reduced nearly quantitatively to 4-phenylbenzohydrol. In the absence of the alcoholate, it was found to be reduced to the pinacol, 4,4′-diphenylbenzopinacol. Several other substituted ketones behaved in accordance with the new mechanism, yielding hydrols. These included 4-methylbenzophenone, 4,4′-dimethylbenzophenone, 4-methoxybenzophenone, 4-chloro-4′-methoxybenzophenone and 4-chlorobenzophenone. The photochemical reduction process as modified by Bachmann [79] is suitable for the preparation of benzopinacol.

Migita [80] finds that di-*p*-methoxybenzophenone in alcohol is reduced in sunlight to the pinacol.

At 100°C., benzophenone itself undergoes no change when irradiated for nine hours by a mercury arc, and acetophenone none after seven hours.[81] When 0.1 molar solutions in hexane or benzene were irradiated, however, benzopinacol crystallized out with a quantum efficiency of 0.04. None was formed when the solvent was carbon tetrachloride.

According to Jenkins,[82] several ketones of the type $C_6H_5COCH_2C_6H_5$ on standing in light and air undergo autoxidation, yielding acids and aldehydes. Thus $C_6H_5CH_2COC_6H_4Cl$-2 gives benzaldehyde and *o*-chlorobenzoic acid.

Paternò and Chieffi [83] observed on exposing benzophenone and phenylacetic acid in benzene to sunlight for five months that benzopinacol and triphenyllactic acid were formed. de Fazi [84] in repeating these experiments always found pressure due to carbon dioxide, on opening the tubes. The reaction of benzophenone with butyric acid also produces carbon dioxide. In the case of the phenylacetic acid reaction, by opening the tube, removing the crystalline deposit of αβ-triphenyl-β-hydroxypropionic acid and benzophenone, and restarting the reaction, successive

[79] Bachmann, W. E., *Organic Syntheses*, New York, John Wiley & Sons, Inc., **14**, 8 (1934).

[80] Migita, M., *Bull. Chem. Soc. Japan*, **7**, 334 (1932); *Chem. Abs.*, **27**, 716 (1933).

[81] Bowen, E. J., and de la Praudière, E., *J. Chem. Soc.*, 1503 (1934).

[82] Jenkins, S. S., *J. Am. Chem. Soc.*, **57**, 2733 (1933).

[83] Paternò, E., and Chieffi, G., *Gazz. chim. ital.*, **40**, II, 321 (1910); *Chem. Abs.*, **5**, 2632 (1911).

[84] de Fazi, R., *Atti accad. Lincei*, **6**, 266 (1925); *Chem. Abs.*, **20**, 594 (1926); *Gazz. chim. ital.*, **57**, 551 (1927); *Atti II congr. naz. chim. pura applicata*, 1287 (1926); *Chem. Abs.*, **22**, 2154 (1928).

deposits of this mixture could be obtained. The course of the reaction is believed to be:

$$(C_6H_5)_2CO + C_6H_5CH_2COOH \longrightarrow (C_6H_5)_2C(OH)\cdot CH(C_6H_5)\cdot COOH$$
$$2C_6H_5CH_2COOH \longrightarrow C_6H_5CH_2CH_2C_6H_5 + 2CO_2 + H_2$$
$$2(C_6H_5)_2CO + H_2 \longrightarrow (C_6H_5)_2C(OH)\cdot C(C_6H_5)_2OH.$$

The ability of benzylphenylacetate to react with benzophenone was believed to account for the fact that only a small amount of this compound could be isolated. Irradiation of a similar mixture of phenylacetic acid, benzophenone and benzene in a quartz tube by a mercury arc for 100 hours gave no triphenyllactic acid and only traces of carbon dioxide. Irradiation with a 2000 C.P. Osram lamp, however, produced abundant quantities of these substances. Exposure of phenylacetic acid alone in benzene to sunlight for six months gave little carbon dioxide and a little of a yellow oil. The Osram lamp gave detectable quantities of carbon dioxide in 24 hours. After 280 hours, there were fairly large quantities of gas and some crystals, probably of *s*-diphenylethane.

4,4′-Tetrachlorodimethylbenzophenone is very sensitive to light and is transformed by it into a plastic mass.[85] A similar behavior was observed in the case of 4,4′-di(hydroxymethyl)benzophenone. The *N*-alkyloximes of benzophenone also resinify and decompose rapidly in ultraviolet light.[86] *β-o*-Nitrophenylethylketone loses a molecule of water on irradiation and gives a substance with acidic properties, which melts about 300°C.[87]

After a week in direct sunlight in a sealed glass tube, an alcoholic solution of *o*-benzophenonecarboxylic acid yielded the dilactone of tetraphenyldihydroxyethanedicarboxylic acid. Similar reactions were given by *p*-tolyl-*o*-benzoic acid and acetophenone-*o*-carboxylic acid.[88] Straus, Muffat and Heitz [89] noted a reaction whereby 1-phenylpyrazolines are obtained by the action of phenylhydrazine on certain aromatic ketones, owing to the extraordinary ease with which the hydrazones first formed rearrange.

From an investigation of diketones, Porter, Ramsperger and Steel [90] find that under the influence of ultraviolet radiation, benzil in the vapor state is decomposed into carbon monoxide and benzophenone when the temperature is 200°C. or more. In dilute alcohol, in the absence of air, it is partly hydrolyzed to benzoic acid and benzaldehyde, but a portion of it is reduced by the alcohol to benzoin. In aqueous alcohol in contact with air, it is converted into benzoic acid. Further oxidation of the latter gives some salicylic acid.

Benzilic acid is not formed in solutions of benzil. The decomposition products of benzilic acid, namely, benzopinacol in the absence of oxygen, and benzophenone and benzopinacol in its presence, were never found in the exposed benzil solutions. Marchlewski and Wyrobek [91] find benzil to absorb strongly with a maximum at 2590A.

[85] Connerade, E., *Bull. soc. chim. Belg.*, **43**, 447 (1934); *Chem. Abs.*, **29**, 768 (1935); *Bull. soc. chim. Belg.*, **42**, 311 (1933); *Chem. Abs.*, **27**, 507 (1933).

[86] Martynoff, M., *Ann. chim.*, **7**, 424 (1937); *Chem. Abs.*, **31**, 4973 (1937). For anisalacetophenone, see Stobbe, H., and Hensel, A., *Ber.*, **59**, 2254 (1926).

[87] Tănăsescu, I., and Tănăsescu, E., *Bull. soc. chim.*, **3**, 865 (1936).

[88] Limaye, D. B., *J. Univ. Bombay*, **1**, Pt. 2, 52 (1932); *Chem. Abs.*, **27**, 2097 (1933).

[89] Straus, F., Muffat, C., and Heitz, W., *Ber.*, **51**, 1457 (1918).

[90] Porter, C. W., Ramsperger, H. C., and Steel, C., *J. Am. Chem. Soc.*, **45**, 1827 (1923).

[91] Marchlewski, L., and Wyrobek, O., *Bull. intern. acad. Polonaise*, **93**, **1929A**; *Chem. Abs.*, **23**, 5405 (1929).

Phenols

The rays of the quartz mercury lamp, according to Gibbs,[92] color pure phenol light red, in the presence of oxygen, with remarkable rapidity (about one minute). Dermatol (bismuth subgallate) on irradiation produces a violet-colored pigment known as galloflavin.[93] Exposure of 3,4-chloronitrosophenol in ethyl alcohol [94] transforms it into resinous products.

The *m*-cresols are said to color more rapidly on exposure to light and air than the *o*- and *p*-cresols, and gentisic acid and its esters are even more readily colored.[96] Viktorin [97] finds the oxidation of phloroglucinol by atmospheric oxygen to evolve ultraviolet radiations.[98] Schweckendiek [99] finds guaiaconic acid, like guaiaretic acid, to be sensitive to light, the sensitivity being increased by the addition of collodion, Zapon lacquer, or a solution of sulfur in carbon disulfide. The product is green and results from an oxidation process. It may be employed as a photographic process, the green image being fixed with a mixture of ammonium acetate and benzene.

Aside from these scattered observations, little definite seems to be known regarding the photochemistry of the phenols. There is, however, much data on their absorption spectra. Indeed, by measurements in solutions containing various amounts of added alkali, it is possible to determine the dissociation constant of phenol by the changes in its absorption spectrum.[100]

Quinones

Because of their importance for theories of color, the visible and ultraviolet absorption spectra of the quinones, especially benzoquinone, have been much investigated. This topic, however, lies beyond the scope of this work. Benzoquinone as vapor exhibits a region of fine band absorption from 4800 to 4200A, one of narrow bands between 3100 and 2600A, and a continuous region at shorter wavelengths.[101]

[92] Gibbs, H. D., *J. Am. Chem. Soc.*, **34**, 1193 (1912).

[93] Guyot, R., *Bull. soc. pharm. Bordeaux*, **66**, 18 (1928); *Chem. Abs.*, **23**, 4015 (1929).

[94] Hodgson, H., and Kershaw, A., *J. Chem. Soc.*, 1553 (1929). Some data on the effects of various wave-lengths on the oxidation of *d*-catechin in the presence of a complex cobalt salt have been recorded by Shibata and Goda.[95]

[95] Shibata and Goda, *Iwata Inst. Plant Biochem., Publ.* **2**, 175 (1936); *Brit. Chem. Abs.*, **A**, 808 (1936).

[96] Gibbs, H. D., Williams, R. R., and Pratt, D. S., *Philippine J. Sci.*, **7**, 79 (1912).

[97] Viktorin, O., *Chem. Listy*, **29**, 245 (1935); *Brit. Chem. Abs.*, **A**, 7 (1936).

[98] In a method of making photographic prints, the sensitive layer may contain a colorless inorganic oxidizing agent such as nitric acid or lithium nitrate, and a cyclic organic amino- compound such as aminophenol, benzidine, dianisidine, etc. These compounds are sensitive only to ultraviolet light which produces colored compounds. After exposure, the unexposed portions may be washed out with water or other solvent, the colored product being insoluble. British P. 413,093, April 20, 1933, to N. V. Philips' Gloeilampenfabriken. *Brit. Chem. Abs.*, **1934B**, 813.

[99] Schweckendiek, C., *Diss.*, Giesen, 1927; *Brit. Chem. Abs.*, **A**, 1041 (1927).

[100] Stenström, M., and Goldsmith, N., *J. Phys. Chem.*, **30**, 1683 (1926); Stenström, M., and Reinhard, M., *J. Phys. Chem.*, **29**, 1477 (1925); Job, P., *Compt. rend.*, **186**, 1546 (1928). For other data on the absorption of phenols, see Kepianka, E., and Marchlewski, L., *Bull. soc. chim.*, **35**, 1613 (1924; Valyashko, N. A., *J. Russ. Phys.-Chem. Soc.*, **58**, 779 (1926); *Chem. Abs.*, **22**, 949 (1928); Purvis, J. E., *Proc. Cambridge Phil. Soc.*, **23**, I, 588 (1927); Conrad-Billroth, H., *Z. physik. Chem.*, **20B**, 222, 227 (1933); Savard, J., *Ann. Chim.*, **9**, 287 (1929); **11**, 287 (1929); *Compt. rend.*, **188**, 782 (1929); Lambrechts, A., *Compt. rend.*, **198**, 1852 (1934); Kepianka, E., and Marchlewski, L., *Bull. intern. acad. Polonaise*, 75, **1926A**; *Bull. soc. chim.*, **39**, 1368 (1926); Goslawski, W., and Marchlewski, L., *Bull. Intern. Acad. Polonaise*, 383 **1931A**; de Boer, J. H., and Custers, J. F. H., *Z. physik. Chem.*, **25B**, 238 (1934); Eisenbrand, J., and von Halban, H., *Z. physik. Chem.*, **146**, 30, 101, 111 (1930); Saint-Maxen, A., and Dureuil, E., *Compt. rend.*, **197**, 1411 (1933); Marchlewski, L., and Wyrobek, O., *Bull. intern. acad. Polonaise*, 93 **1929A**.

[101] Lifschitz, I., and Rosenbohm, E., *Z. Physik*, **38**, 61 (1926); Light, L., *Z. physik. Chem.*, **122**, 414 (1926).

Benzoquinone in light effects the oxidation of various alcohols. Leighton and Forbes[102] found that when water was also present in large amounts, the reaction exhibited an induction period during which a dimer of the quinone was believed to be formed. When the solvent was 50-per cent alcohol, there was no inhibition. With wave-lengths shorter than 4350A, they found the quantum yield to be 0.5 in alcohol and in aqueous alcoholic solutions. It was independent of the wave-length, and in aqueous alcoholic solutions, also of the concentrations. With longer wave-lengths the quantum yields decreased, indicating the existence of a threshold inside the first absorption band. As the concentration of alcohol was decreased, the threshold was displaced toward shorter wave-lengths. These investigators suggested that every absorbed quantum might produce activation, the observed quantum yields being lowered by a secondary reaction which has an efficiency of but 50 per cent. Recently, these results have been challenged by Berthoud and Porret[103] who observed quantum yields of unity at 4050, 4080 and 4360A. They found the rates to be independent of the quinone concentration and temperature. The rates decrease slowly with decreasing alcohol concentration, and are proportional to the light intensity. Similar results were obtained with isopropyl alcohol.

The oxidation of ferrous sulfate by benzoquinone, but not the reverse process, is sensitive to light. It proceeds with a quantum yield of unity at 4050, 4080 and 4360A and is independent of the temperature and concentrations of reactants.[104]

Aromatic Acids and Their Derivatives

Benzoic Acid. Kailan[105] found ultraviolet irradiation of aqueous solutions of benzoic acid to yield reducing substances, formic acid and oxalic acid. The velocity of the formation of these substances increased as the square of the concentration. Alcoholic solutions are esterfied[106] to the extent of 30 per cent in eight days. The rate is promoted by the presence of a trace of hydrochloric acid.

On exposure to acid and sunlight, the esters of the three hydroxybenzoic acids color more rapidly than the free acids; the *meta* compounds are the most rapidly changed; the *para* compounds are practically unaffected.[107]

Decomposition of acetylbenzoyl peroxide by ultraviolet light yields carbon dioxide, toluene, methyl benzoate, methane, phenyl benzoate and complex materials of acid and neutral character.[108] Possibly hydrolysis occurs, the necessary water being liberated in the formation of the complex materials.

$$2CH_3COO_2COC_6H_5 + H_2O \longrightarrow C_6H_5COO_2COC_6H_5 + CH_3COOOH + CH_3COOH.$$

Fichter and Schnider[109] found the decomposition of dibenzoyl peroxide in ultraviolet light to yield about 80 per cent of the theoretical quantity of carbon dioxide and diphenyl. The residue, an amorphous resin, was not characterized.

Absorption of potassium cyanide by benzaldehyde in the benzoin condensation is unaffected by irradiation.[110] Benzoin, however, is converted into a viscous resin by irradiation, the process being favored by an increase in temperature.

[102] Leighton, P. A., and Forbes, G. S., *J. Am. Chem. Soc.*, **51**, 3549 (1929); for the actinometric use of benzoquinone, see Chapter 7.
[103] Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 694 (1934).
[104] Porret, D., *Helv. Chim. Acta*, **17**, 703 (1934).
[105] Kailan, A., *Z. physik. Chem.*, **95**, 215 (1920); *J. Chem. Soc.*, **118**, ii, 576 (1920).
[106] Stoermer, R., and Ladewig, H., *Ber.*, **47**, 1803 (1914).
[107] Gibbs, H. D., Williams, R. R., and Pratt, D. S., *Philippine J. Sci.*, **7**, 79 (1912).
[108] Fichter, F., and Willi, E., *Helv. Chim. Acta*, **17**, 1173 (1934).
[109] Fichter, F., and Schnider, A., *Helv. Chim. Acta*, **13**, 1428 (1930).
[110] Bousset, R., *Bull. soc. chim.*, **2**, 309 (1935).

Salicylic Acid. Little is known of the photochemical behavior of this acid. Light (but not ultraviolet light) is said to darken the pharmaceutical solutions of sodium salicylate containing sodium bicarbonate. This probably consists in an oxidation with the formation of quinones.[111] Methyl salicylate becomes colored on exposure to air and sunlight, the tint varying from light yellow for short exposures to reddish-brown for protracted ones.[112]

It has been proposed to use such aryl azides as azido-salicylic acid (prepared by the action of sodium azide on diazosalicylic acid) in photographic processes. A layer of the material incorporated in gelatin and exposed under a negative forms a dye, after which the unchanged azide may be washed out.[113]

Of 22 anils known to be phototropic, 15 were said to be derivatives of salicylaldehyde. Recently Brewster and Millam[114] have added three, one a derivative of salicylaldehyde and the other two of 5-bromosalicylaldehyde.

Mandelic Acid. This acid can be oxidized by methylene blue by wave-lengths in the range 2540 to 4360A if uranyl nitrate is employed as photosensitizer. In the mechanism suggested by Ghosh, Narayanamurthi and Roy,[115] excited UO_2'' ions yield their energy to mandelic acid, which is decomposed with the production of benzaldehyde, carbon dioxide, water and the UO″ ion. The latter takes an oxygen atom from water, the hydrogen of which reduces methylene blue to the leuco-compound. Oxygen restores the methylene blue, and light excites the uranyl ion so that the processes may be repeated.

Phthalates. When lead phthalate is exposed in a small quartz crucible to ultraviolet rays, the outer layer decomposes rapidly with the formation of a yellowish-brown substance of unknown composition, but probably containing lead oxide. Under the same conditions mercury phthalate is unaffected.[116]

Jaeger[117] claims the decarboxylation of polycarboxylic acids, for example, the conversion of phthalic into benzoic, by subjecting them at 300° to 420°C. in the presence of reducing gases (hydrogen or water gas) to various types of electrical discharge, ultraviolet light, cathode rays or x-rays.

For refining liquid alkyl esters derived from acids produced by the catalytic oxidation of aromatic hydrocarbons, such as dibutyl phthalate, so that distillation of the ester is rendered unnecessary, and its color improved, the material may be exposed to the action of ultraviolet light.[118]

An alcoholic solution of 2,4-dihydroisophthalic acid, which appears to react as a quinone derivative, forms acetaldehyde in sunlight.[119]

Although terephthaldehyde is very stable in the solid state and in solution in benzene in darkness, Suida[120] finds that its solution undergoes rapid atmospheric oxidation when irradiated by a mercury lamp, a white crystalline deposit being formed. This consists of terephthaldehydic acid to the extent of roughly two-thirds, the remainder being terephthalic acid. The solution from which the crystals have separated gives a peroxide reaction with acidified potassium iodide solution.

[111] Krantz, J. C., Jr., *J. Am. Pharm. Assoc.*, **17**, 1203 (1928); Liberalli, C. H., *Bol. assoc. brasil. farm.*, **16**, 154 (1935); Chem. Abs., **29**, 5989 (1935).
[112] Stoermer, R., and Ladewig, H., *Ber.*, **47**, 1803 (1914).
[113] British P. 333,820, Nov. 3, 1928, to Kalle and Co. *Brit. Chem. Abs.*, **1930B**, 1092.
[114] Brewster, C. M., and Millam, L. H., *J. Am. Chem. Soc.*, **55**, 763 (1933).
[115] Ghosh, J. C., Narayanamurthi, D. S., and Roy, N. K., *Z. physik. Chem.*, **29B**, 236 (1935).
[116] Ekeley, J. B., and Banta, C., *J. Am. Chem. Soc.*, **39**, 762 (1917).
[117] Jaeger, A. O., U. S. P. 1,909,357, May 16, 1933, to Selden Co.; *Brit. Chem. Abs.*, **1934B**, 87.
[118] Smith, F. D., U. S. P. 1,948,281, Feb. 20, 1934 (to Monsanto Chemical Co.); *Chem. Abs.*, **28**, 2725 (1934).
[119] Marzin, A., *J. prakt. Chem.*, **138**, 107 (1933); *Chem. Abs.*, **27**, 5317 (1933).
[120] Suida, H., *Monatsh.*, **33**, 1173 (1912); *J. Chem. Soc.*, **104** (i), 52 (1913).

The oxidation is not accelerated by the presence of nitrobenzene, which, indeed, exerts a hindering effect. A comparison with benzaldehyde seems to indicate that, assuming the supply of oxygen by diffusion to be more than sufficient, the oxidation velocity of each aldehyde group in terephthaldehyde is considerably diminished by the presence of a similar group in the *para* position. Spectrographic examination indicates that the effective rays are those of wave-lengths between 4000 and 3000A, but yellow and red light can cause the oxidation to occur, although only very feebly.

Cinnamic Aldehyde and Cinnamic Acid. These compounds exhibit interesting photochemical reactions because, in addition to the features common to the aldehydes and acids, the presence of a double bond in the side chain offers new possibilities of polymerization and stereoisomerization. Cinnamic acid, in alcoholic solution, exhibits one broad absorption band with a maximum at 2710A. Hydrocinnamic acid, however, in aqueous solution, shows two bands with maxima at 2670 and 2580A.[121]

In sunlight, cinnamic aldehyde reacts with quinone as do other aldehydes. Bargellini and Monti[122] exposed 10.8 gm. of quinone and 13.2 gm. of cinnamic aldehyde in 100 cc. of benzene in a sealed tube for one month. The quinone was reduced to hydroquinone and the aldehyde oxidized to cinnamic acid. These two products then combined, the reaction being analogous to that between phenanthrenequinone and certain aldehydes described by Klinger.[123] According to Stoermer and Ladewig,[124] in the presence of a trace of hydrochloric acid, cinnamic acid reacts with alcohol when irradiated, as much as 37 per cent being esterified in eight days.

When thin layers of finely powdered *o*-nitrocinnamic acid are exposed to sunlight, a red substance melting at 120°C. is produced. It is probably hydroxyisatogenic acid, $C_6H_4\begin{cases}CH\cdot OH\\ \diagdown\\ C\cdot COOH\\ \diagup\\ NO\end{cases}$. This is another[125] example of a type of reaction frequently encountered.

The presence of a double bond in the side chain of cinnamic acid permits the existence of *cis* and *trans* forms. Photochemical changes may consist of either a stereoisomerism or a polymerization of either form to a dimer. This, together with the fact that *allo*-(*cis*)-cinnamic acid[125a] is trimorphous, having forms melting at 42°, 58° and 68°C., makes the photochemistry of this compound an intricate subject which has been much investigated, with confusing results. Since the matter is rather highly specialized, space does not permit a complete discussion.[126]

Stoermer[127] showed that ultraviolet light changes the less fusible stable to the more reactive labile forms. The extent of the transformation was thought to be dependent upon the energy differences between the steroisomers. Many derivatives of cinnamic acid were studied[128] and it was believed that in most cases an

[121] Marchlewski, L., and Wyrobek, O., *Bull. acad. Polonaise,* 331 **(1929)**; *Chem. Abs.,* **24,** 3711 (1930). Ley, H., and Dreinhöfer, R., *Z. wiss. Phot.,* **29,** 134 (1930); Ramart-Lucas and Trivédi, R., *Compt. rend.,* **195,** 783 (1932); Purvis, J. E., *J. Chem. Soc.,* 780 **(1927)**.

[122] Bargellini, G., and Monti, L., *Gazz. chim. ital.,* **60,** 474 (1930); *Chem. Abs.,* **25,** 96 (1931).

[123] Klinger, H., *Annalen,* **249,** 137 (1888); **382,** 211 (1911); *Ber.,* **24,** 1340 (1891); **31,** 1214 (1898). In most of this work many of the quinone reactions followed a different course.

[124] Stoermer, R., and Ladewig, H., *Ber.,* **47,** 1803 (1914).

[125] Tănăsescu, I., *Bull. soc. chim.,* **41,** 1074 (1927).

[125a] The ordinary *trans*-cinnamic acid melts at 133°C.

[126] de Jong, A. W. K., *Chem. Weekblad,* **26,** 270 (1929) has compiled a large number of references regarding the effects of sunlight on the *cis*- and *trans*-cinnamic acids.

[127] Stoermer, R., *Ber.,* **42,** 4865 (1909); *J. Chem. Soc.,* **8** (ii), 114 (1910).

[128] Stoermer, R., with Frederici, Brautigam and Neckel, *Ber.,* **44,** 637 (1911).

equilibrium was attained. The number after each of the following compounds represents the percentage of the less fusible form which, at equilibrium, has been transformed: methyl-*o*-nitro-*o*-methoxycinnamate, 80; *p*-methoxycinnamic acid, 25; sodium-*o*-chlorocinnamate, 10; *o*-anisylcinnamic acid, 35-40; *o*-anisylcinnamide, 70; *o*-anisylcinnam-methylamide, 36; and the corresponding ethylamide, 40; β-*o*-anisyl-α-methylcinnamic acid, 5, and the corresponding amide, 5; the form of cinnamic acid melting at 42°C., 30-40. In the case of *o*-chlorocinnamic acid, when glacial acetic acid was employed as solvent, it was observed that, in addition to the expected isomerization, part of the acid combined with the solvent.

When daylight or sunlight, rather than the light of the mercury arc is used, polymerization reactions also occur with the formation of dimers[129] although isomerization occurs with either sunlight or mercury arc light. Fused *cis*-cinnamic acid is transformed extensively to the *trans* form after 96 hours of mercury arc irradiation. Similarly, α-*trans*-cinnamic acid, fused or in solution, isomerized to the equilibrium mixture. For this change, radiations of wave-length 3200 to 2700A are most effective. The reaction is greatly accelerated by the addition of hydrochloric acid.

When the solid acids or their aqueous suspensions are exposed to sunlight, this change is accompanied by polymerization; α-*trans*-cinnamic acid yields mainly the dimer α-truxillic acid with a little β-truxinic acid. *Allo*-cinnamic acid (*cis*) yields as its polymerization product chiefly β-truxinic acid, together with the isomerization product *trans*-cinnamic acid and its dimer, a little α-truxillic acid. The latter change took place to the extent of 71 per cent after 196 hours in sunlight, but after 200 hours of the mercury arc irradiation only to the extent of 4.4 per cent. Very similar results were recorded for the polymerization of the *trans* acid. Long ultraviolet rays accordingly favor polymerization, but the shorter ones hinder it and exert a depolymerizing action on truxinic and truxillic acids. Each dimer when irradiated by the shorter radiations depolymerizes to the monomer from which it is originally formed by the longer rays.

The metastable β-form of *trans*-cinnamic acid is much more readily isomerized than the stable α-*trans*-cinnamic acid which therefore yields on polymerization but little β-truxinic acid and much α-truxillic acid.

Experiments of this type are further complicated by the fact that some autoxidation to benzaldehyde and in some cases to benzoic acid also occurs. On long illumination of *trans*-cinnamic acid the yield of the dimer, α-truxillic acid, decreases and that of benzaldehyde increases. Analogous results are obtained in the irradiation of *cis*-cinnamic acid.

Stobbe and Zschoch[130] found that the monomeric *trans*-cinnamic acid in 0.0001*N* alcoholic solution absorbs light strongly, although its saturated dimer, α-truxillic acid, is almost completely transparent and begins to absorb only in a 40-mm. layer of a 0.001*N* solution. In a 10-mm. layer of 0.01*N* solutions, its end absorption begins at a wave-length about 600A units shorter than that of the monomer. This difference in absorption accounts for the differing effects of longer and shorter ultraviolet radiations on polymerization and depolymerization. These compounds do not fluoresce.

The quantum yields for the isomerization by the 3130A line have been found to

[129] Stobbe, H., *Ber.,* **52B,** 666 (1919); Stobbe, H., and Steinberger, F. K., *Ber.,* **55B,** 2225 (1922). See also de Jong, A. W. K., *Chem. Abs.,* **16,** 2683 (1922); **6,** 2746 (1912); Stoermer, R., and Scholtz, F., *Chem. Abs.,* **15,** 1888 (1921) and Stobbe, H., and Lehfeldt, A., *Ber.,* **58B,** 2415 (1925).

[130] Stobbe, H., and Zschoch, F., *Ber.,* **60B,** 457 (1927).

be as follows: Cinnamic acid, 0.003 molar, 0.61; 0.002 molar, 0.53; isocinnamic acid, 0.003 molar, 0.21; 0.002 molar, 0.15.[131]

Various derivatives of cinnamic acid are subject to similar transformations. Stobbe[132] observed methyl *trans*-cinnamate to be converted to a small extent by six months of exposure to sunlight into methyl α-truxillate (2.9 per cent) derived from the solid ester and 0.2 per cent of Liebermann's polyester formed from portions which had been melted by the heat of the sun. The remainder was unchanged. *trans*-Cinnamide was in five months converted into α-truxilldiamide to the extent of 75 per cent. *trans*-Cinnamanilide remains unchanged after six months' exposure in the solid state or suspended in hydrochloric acid. *allo*-Cinnamic anhydride is converted into a mixture of 80 per cent *trans*-cinnamic anhydride remains unchanged, aside from slight resin formation. Cinnamaldehyde, after eight months in sunlight, yields a mixture of 60 per cent unchanged aldehyde, 33 per cent cinnamic acid and 7 per cent polycinnamaldehyde, apparently a tetramer, which does not yield an oxime or react with ammoniacal silver nitrate or Schiff's reagent. At least 91 per cent of α-bromocinnamic acid remains unchanged after seven months in sunlight or 375 hours in the light of a mercury vapor lamp; the remainder is converted by autoxidation into oxalic acid, benzoic acid and free bromine. No polymerization or resin formation occurred. Gulland and Virden[133] find the yellow *trans*-2-amino acid obtained by the reduction of 3,4,2′,5′-tetramethoxy-2-nitro-*trans*-α-phenylcinnamic acid, in alcoholic solution to give after several days in ultraviolet light, 7,8,2′,5′-tetramethoxy-3-phenylcarbostyril. The action of ultraviolet light on the sodium salt of *trans*-2-nitro-3,4,2′,5′-tetramethoxy-α-phenylcinnamic acid gives a small yield of the *cis* form.

o-Hydroxycinnamic acid is oxidized by peracetic acid in darkness to *cis-cis*-muconic acid in very small amount; in light a more or less complete isomerization to the *trans-trans* acid occurs.[134] *cis-cis*-Muconic acid, in 96 per cent alcohol with a trace of iodine, is almost quantitatively rearranged into the *trans-trans* compound.

Acids containing the cinnamylidene residue and their nitriles have also been extensively investigated. Solutions of α-phenylcinnamylideneacetonitrile in benzene or chloroform in either the presence or absence of iodine in sunlight form two dimers, one melting at 197°C. and the other at 215°C.[135] The former is 1,3-diphenylcyclobutane-2,4-diatroponitrile, also called 1,3-diphenyl-2,4-*bis*-(β-phenyl-β-cyanovinyl)cyclobutane:

$$CN - C\cdot C_6H_5 = CH\cdot CH{<}\begin{matrix}CHC_6H_5\\CHC_6H_5\end{matrix}{>}CH - CH = C\cdot(C_6H_5)CN.$$

The isomerism of the two dimers may be of the *cis-trans* type, depending on a difference of location of the phenyl and cyano- groups at one or both of the double bonds of the side chain, since on treatment with permanganate both yield α-truxillic acid.

According to Lohaus,[136] exposure of a solution of the stable ethyl cinnamylidenecyanoacetate in ethyl alcohol in the presence of a little sulfuric acid gives after one day in sunlight a labile form. Further exposure of the crystalline material recovered yields a cyclobutane derivative previously described by Reimer (1911, 1913). In the absence of sulfuric acid, however, the original compound polymerizes to an open-chain dimer, melting at 165°C. The labile form of ethyl cinnamylidene cyanoacetate is rapidly converted into its stable form when its alcoholic solution, containing iodine, is exposed to sunlight in quartz vessels.

allo-(*trans,cis*)-Cinnamylideneacetic acid is converted into the normal (*trans-trans*) form by irradiation of its solutions in the presence of iodine.[137] Equilibrium is attained when 90-per cent conversion has been effected, this equilibrium being independent of the concentration of iodine and the intensity of the light and but little dependent on the temperature. Constant unimolecular rate constants could be obtained when concentrations of iodine greater than 0.024*N* were used, but at lower concentrations the rate

[131] Vaidya, B. M., *Proc. Roy. Soc.*, **A129**, 299 (1930).
[132] Stobbe, H., *Ber.*, **58B**, 2859 (1925); *Chem. Abs.*, **20**, 1612 (1926).
[133] Gulland, J. M., and Virden, C. J., *J. Chem. Soc.*, 1478 (**1928**).
[134] Grundmann, C., and Trischmann, H., *Ber.*, **B69**, 1755 (1936); *Chem. Abs.*, **30**, 6354 (1936).
[135] Stobbe, H., and Kuhrmann, F., *Ber.*, **58B**, 85 (1925); *J. Chem. Soc.*, **128**, I, 253 (1925).
[136] Lohaus, H., *Annalen*, **514**, 137 (1934); *Chem. Abs.*, **29**, 1796 (1935).
[137] Ghosh, J. C., and Mitra, M. N., *J. Indian Chem. Soc.*, **3**, 273 (1926); *Brit. Chem. Abs.*, **1927A**, 560.

constant for the forward reaction showed a gradual increase with time indicative of an induction period. This was observed only when freshly prepared solutions were used. With increasing iodine concentrations the rate constant passed through a maximum. The values of the constants decreased with increasing initial concentrations of the compound. They were proportional to the intensity of the light (5000A). A quantum yield of 423 was found. Green light was most effective, then blue, yellow and red light.[138] The rates were highest in methanol, and decreased in other solvents in the order ethanol, mixtures of ethanol and water, and mixtures of chloroform and methanol. In chloroform the rates were very low in comparison with those in solutions containing the hydroxyl group. For benzene or chloroform as solvents Ghosh, Murthi and Das-Gupta[139] have suggested the following reactions as entering the mechanism, in which A represents the *allo*-acid employed and B the normal acid formed.

$$I_2 + h\nu \longrightarrow I + I$$
$$I + A \longrightarrow IA$$
$$IA \longrightarrow I + B$$
$$I + B \longrightarrow IB$$
$$IB + A \longrightarrow I + B + B.$$

They also find that the rate constant increases with the light intensity, at first rapidly and then more slowly; it also varies with the square root of the energy absorbed.

Vorländer and Gieseler[140] find that exposure of a solution of the sodium salt of *trans-trans-p*-methoxycinnamylideneacetic acid to ultraviolet light causes the formation of salts of two acids (or mixtures of acids), melting at 90-96° and 106-110°C., respectively. Both of these regenerate the original acid when their benzene solutions with iodine are exposed to sunlight. Under these conditions, *allo-p*-methoxycinnamylideneacetic acid is converted into the *trans-trans* form. Cinnamylidene-*m*-nitroacetophenone yields, in 10-per cent chloroform solution after 15 days in sunlight or 12 hours in ultraviolet from a mercury lamp, a semisolid substance which slowly forms a resin with a fracture like that of colophony.[141] In this resinification, it differs from cinnamylideneacetophenone, which polymerizes under the action of light.[142]

The ability of dicinnamalacetone to form insoluble, noncrystalline products on exposure to light when exposed in a layer with shellac and a basic dye has led Seymour[143] to propose its use in photographically printing dyed relief images.[144]

The photochemical addition of bromine to α-phenylcinnamonitrile[145] under conditions of slight absorption of light proceeds at a rate proportional to the square root of the intensity and to the 1.5 power of the bromine concentration. Under conditions of total absorption, it is proportional to the square root of the intensity and to the bromine concentration. The temperature coefficient is 1.4. The dibromide, once formed, can also be photochemically decomposed in the presence of bromine, which acts as a sensitizer. The rate is retarded by the presence of a large excess of the nitrile.

Halogenation of Cinnamic Acid. The rate of photobromination of cinnamic acid is dependent upon the form of the acid employed. The thermal rate for *allo*-cinnamic acid, melting at 68°C., is increased five-fold by yellow light, but that of the ordinary acid (melting 133°C.) is increased forty-fold.[146] In darkness, the

[138] Ghosh, J. C., Das Gupta, D. N., Roy, N. C., and Chatterjee, H. K., *J. Phys. Chem.*, **34**, 2771 (1930).
[139] Ghosh, J. C., Murthi, D. S. N., and Das Gupta, D. N., *Z. physik. Chem.*, **B26**, 255, 267 (1934).
[140] Vorländer, D., and Gieseler, K., *J. prakt. Chem.*, **121**, 247 (1929); *Chem. Abs.*, **23**, 3912 (1929).
[141] Giua, M., *Gazz. chim. ital.*, **55**, 567 (1925); *Chem. Abs.*, **20**, 749 (1926).
[142] Stobbe, H., and Rücker, C., *Ber.*, **44**, 869 (1911); *Chem. Abs.*, **5**, 2253 (1911).
[143] Seymour, M. W., U. S. P. 2,063,348, Dec. 8, 1936, to Eastman Kodak Co.; *Chem. Abs.*, **31**, 621 (1937).
[144] For a study of the photodimers of cinnamalmalonic acid, see Stobbe, H., Hensel, A., and Simon, W., *J. prakt. Chem.*, **110**, 129 (1925).
[145] Berthoud, A., and Nicolet, G., *Helv. Chim. Acta*, **10**, 417 (1927); *J. chim. phys.*, **25**, 40 (1928).
[146] Meyer, J., and Pukall, W., *Z. physik. Chem.*, **A145**, 360 (1929); see also Padoa, M., and Vita, N., *Gazz. chim. ital.*, **58**, 3 (1928).

rate of bromination of the *allo*-acid melting at 58°C. is greater than that of the form melting at 68°, but the form melting at 42°C. is more rapidly brominated than either of these. These differences led Meyer and Pukall to regard the three forms of the *allo*-acid as isomers, unexplained by ordinary stereochemical concepts, rather than as polymorphs. They were unable to obtain constant rate values by the use of yellow, blue or yellowish white light and the 133°C. ordinary cinnamic acid, but with red or green light found the reaction to be bimolecular.

Yajnik and Uppal[147] found that, for equimolar concentrations of bromine and cinnamic acid in either carbon disulfide, carbon tetrachloride or chloroform, the formula for unimolecular reactions gave sufficiently constant values for the rate constant. A temperature coefficient of 2.8, increasing with the wave-length used, was observed by Ghosh and Purkayastha,[148] who found the velocity coefficient independent of the concentration of bromine. It increased with the initial concentration of the cinnamic acid and varied as the square root of the intensity of incident blue light. For green light, the increase was greater. They found that there was an induction period and an after-effect, from which they assumed the existence of a complex intermediate. Excited bromine molecules were considered to function in the mechanism. One quantum of light was observed to form 426 molecules of dibromophenylpropionic acid in one experiment. Other values were, in carbon tetrachloride, 22 at 5330A and 43 at 4880A, and in carbon disulfide, 101 and 156, respectively. Berthoud and Béraneck[149] believed the velocity in carbon tetrachloride to be affected by an unknown catalyst, the effect of which they could not completely eliminate. They differed from the Indian workers in finding the reaction independent of the concentration of acceptors, such as cinnamic acid. With strong absorption, it was nearly first order with respect to bromine, but with weak absorption, it was of 3/2 order. The quantum yield was about 36 with a violet filter and 10 with a green filter. Rotating sectors, transmitting 50 and 25 per cent of the light, reduced the velocity to 65 and 43 per cent. This use of sectors has been criticized by the Indian workers. The mechanism of Berthoud assumes that bromine atoms participate in reaction chains.

$$A + Br \longrightarrow ABr.$$
$$ABr + Br_2 \longrightarrow ABr_2 + Br.$$

Ghosh, Bhattacharya and Murthi[150] find the combined effect of any two radiations selected from 546, 436 and 406 mμ to be less than the sum of the two separate effects.

Bauer and Daniels[151] confirmed the chain nature of the reaction but found much lower quantum yields, 1 to 15 or more, varying with the concentration of the bromine and the temperature. The yields decrease linearly with dilution to unity at infinite dilution. The nature of the reaction was thought to be complex since, in addition to the primary process with a quantum yield of unity, it involved also a photo-excited thermal reaction which can be suppressed by the use of low

[147] Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Brit. Chem. Abs.*, **1930A**, 174. See also Mathur, K. G., Gupta, R. S., and Bhatnagar, S. S., *Indian J. Physics*, **2**, 243 (1928) and Berthoud, A., *J. chim. phys.*, **26**, 435 (1929).

[148] Ghosh, J. C., and Purkayastha, R. M., *J. Indian Chem. Soc.*, **2**, 261 (1925); *Chem. Abs.*, **20**, 1953 (1926); *Quart. J. Indian Chem. Soc.*, **4**, 409, 553 (1927); *Brit. Chem. Abs.*, **1928A**, 172, 256.

[149] Berthoud A., and Béraneck, J., *J. chim. phys.* **24**, 213 (1927); *Helv. Chim. Acta*, **10**, 289 (1927).

[150] Ghosh, J. C., Bhattacharya, S. K., and Murthi, M. L. N., *J. Indian Chem. Soc.*, **14**, 452 (1937); *Chem. Abs.*, **32**, 4881 (1938).

[151] Bauer, W. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 378 (1934); **56**, 2014, 2564 (1934); see also Ghosh and Purkayastha, *J. Indian Chem. Soc.*, 235 **(1933)**, and Ogg, R. A., Jr., *J. Am. Chem. Soc.*, **58**, 607 (1936).

bromine concentrations and low temperatures. They believed that this reaction forms an example of an energy chain carried by activated bromine molecules.

In ether in diffuse sunlight at −10°, cinnamic aldehyde adds the theoretical amount of bromine, but in brighter light, substitution also occurs. *trans*-Cinnamic acid in sunlight added practically the theoretical amount.[152] *m*-Methoxycinnamic acid in boiling carbon tetrachloride gave α,β-dibromo-β, 3-methoxyphenylpropionic acid. In darkness in acetic acid, there is a quantitative yield of the 6-brom-derivative of the cinnamic acid and this is also formed in boiling acetic acid in sunlight. In boiling chloroform, a mixture of the two products forms. Analogous results are found with the ethyl ester in these solvents. 6-Brom-derivatives of the methoxycinnamic acid, on bromination in carbon tetrachloride in sunlight give the β-6-bromo-derivative of the propionic acid. α-Bromo-*m*-methoxy-*allo*-cinnamic acid is transformed into α-bromo-*m*-methoxycinnamic acid (the *trans* form) by sunlight.

For the chlorination of cinnamic acid, Basu[153] found, in carbon tetrachloride exposed to the full radiation from a quartz lamp, at 22.6°C., a unimolecular rate constant of 3.8×10^{-3}, with respect to chlorine. It was unaffected by changes in the cinnamic acid concentrations. In darkness, there was a constant of 4×10^{-5}. At the wave-lengths 3665, 4040 and 4360A, the quantum yields were 7, 4, and 2. Since no fluorescence could be observed, Basu proposed a mechanism involving, of the chlorine atoms produced in the primary process, only the excited ones as carriers of the chains. The chain length was thought to depend upon the amount of energy associated with the intermediary monochloride of cinnamic acid. Berthoud and Porret[154] believed this reaction to follow the same laws as the photobromination. The life of a reaction chain was considered to be less than 0.02 second. The quantum yields varied with the experimental conditions, being 2.4 in one case. The rate was independent of the concentration of acid, and proportional to the chlorine concentration for total absorption, or to the two-thirds power for weak absorption. It was also proportional to the square root of the light intensity.

Woods and Poulter[155] believed they had demonstrated the ability of ultraviolet light to alter slightly the polarity of the double bond in cinnamic acid. When its solution in absolute ether was irradiated for an hour with the highly polar reagent hydrogen bromide, the residue after evaporation of the ether yielded to ligroin a small portion of material which on recovery from the solvent melted at about 50°C. and had physical properties very similar to those of the compound $C_6H_5CH_2$-CHBrCOOH.[156]

Coumarin, the inner lactone of *o*-hydroxycinnamic acid, also possesses a double bond and is subject to reactions analagous to those of cinnamic acid. It exhibits two absorption maxima at 3200 and 3600A[157] but when one or two hydroxyl groups are introduced into the benzene ring, the resulting products show only one absorption maximum. It has been found that when certain immature plants, which when mature contain coumarin, are irradiated by a mercury-vapor lamp, the odor of coumarin becomes perceptible in a few minutes.[158]

[152] Duquenois, P., *Bull soc. chim.*, **4**, 193 (1937).

[153] Basu, K. P., *J. Indian Chem. Soc.*, **6**, 341 (1929); *Chem. Abs.*, **24**, 784 (1930).

[154] Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 237 (1934).

[155] Woods, G. M., and Poulter, T. C., *Proc. Iowa Acad. Sci.*, **35**, 217 (1928); *Chem. Abs.*, **24**, 1101 (1930).

[156] For data on the photobromination of α-phenylcinnamic acid, see Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 1548 (1934).

[157] Tasaki, T., *Acta. Phytochim*, **3**, 21 (1927); *Chem. Abs.*, **22**, 1543 (1928).

[158] Pougnet, J., *Compt. rend.*, **151**, 355, 566 (1910).

The photobromination of coumarin attains an equilibrium similar to that described by Berthoud and Nicolet for phenylcinnamonitrile. The rate of bromination is greater in carbon tetrachloride than in chloroform, but the reverse is true of the thermal reaction. Williams[159] finds that in ultraviolet light and with 60 molar concentrations of coumarin and bromine, an equilibrium results in 25 minutes in carbon tetrachloride at which time 85.6 per cent of the bromine had reacted. In chloroform, 65.8 per cent had reacted at equilibrium, reached in 45 minutes.

Considerable work has been done on the geometrical photoisomerizations of coumarin and its derivatives. Although Perkin had noted the conversion of methylcoumarinic acid into methylcoumaric acid by sunlight, Stoermer[160] found the tendency the other way in the coumaric acid series, the stable form changing to the labile in ultraviolet rays. Coumaric acid yields 75 per cent of coumarin, and methylcoumaric acid yields 75 per cent of methylcoumarinic acid, while ethylcoumaric acid and acetylcoumaric acid are quantitatively changed to the corresponding coumarinic acids. Benzene or alcoholic solutions were used. Vaidya[161] found the following quantum yields (3130A) for the transformation of coumaric acid: 0.005 molar, 0.031; 0.002 molar, 0.023.

Dey, Rao and Seshadri[162] have pointed out that the esters undergo inversion more readily than the acids. The presence of a nitro- group in the benzene ring accelerates the transformation of both acids and esters but a methoxyl group has the opposite effect. An alcoholic solution of *o*-coumaric acid formed coumarin in 48-per cent yield after six hours of exposure to light and 65-per cent after 24 hours. The methyl and ethyl esters underwent 87- and 74-per cent conversion in 24 hours. Ordinary sunlight supplies the requisite energy for the transformation of the *trans* forms of the coumaric acids and their esters into the *cis* form with higher energy content.

Other Aromatic Compounds with Double Bonds in a Side Chain

Styrenes. Smakula[163] measured the absorption spectra of a number of polystyrenes of molecular weights 3,900 to 240,000. All showed an absorption band at 2600A, the intensity of which increased directly with the molecular weight. A comparison of their spectra with those of styrene and of ethylbenzene showed that the absorption bands belong to the phenyl radicals.

Obviously, stereoisomeric forms of styrene, phenylethylene, cannot exist because of the symmetry of the CH_2. The possibility of photoreaction is therefore limited to polymerization. Stobbe[164] found that an equilibrium is set up between styrene and metastyrene. Styrene solution (5 per cent) showed the following changes in refractive index after 0, 20, 32, 95 and 230 hours of irradiation in Uviol tubes: 1.49883, 1.49911, 1.49939, 1.4994, 1.4994. Metastyrene showed the values: 1.50125, 1.50125, 1.50125, 1.50116, 1.50116. The irradiated solution of styrene gave a precipitate of metastyrene with alcohol; that of metastyrene decolorized permanganate, but the solutions kept in darkness did not.

Taylor and Vernon[165] found the photopolymerization could be accelerated by previous storage of the styrene in contact with oxygen. After 144 hours in contact with hydrogen, styrene polymerized when irradiated in Pyrex at a rate of 5.85 per cent per hour. When stored with oxygen, the rates were at the start, 6.39 per cent; 48 hours, 9.14 per cent; 96 hours, 9.15 per cent and 144 hours, 10.25 per cent per hour. Over oxygen, however, there is both oxidation as well as polymerization. To obtain the true rate of polymerization, hydrogen-distilled samples must be used. The temperature coefficient of polymerization is 1.33 per 10° between 30° and 70° and slightly less, 1.27, between 70° and 100°C. From viscosity measurements it seems that the aggregates formed at higher temperatures were of much larger size than those formed at low temperatures. Quantum yields of 4 at 3000 to 4000A and 7.4 at 2536A indicate a chain mechanism. Hydroquinone inhibits the change, partly by internal filtering and partly by deactivating collisions.

A low-boiling form of nitro-ω-bromostyrene, in which stereoisomerism is possible, is converted into a high boiling form by exposure to ultraviolet light.[166]

bis-Distyrylketone is, according to Stobbe, Färber and Rau,[167] readily depolymerized to distyrylketone in the light of a mercury vapor lamp. Di-*p*-methoxystyrylketone is polymerized, but its addition compounds with uranyl chloride or stannic chloride do not appear to yield a dimer when exposed to light. Methyl-γ-ketopentadienedicarboxylate

$$\begin{array}{l} COOCH_3—CH—CH—CO—CH—CH—COOCH_3 \\ \qquad\qquad\quad | \quad\quad | \quad\quad | \quad\quad | \\ COOCH_3—CH—CH—CO—CH—CH—COOCH_3 \end{array}$$

is readily converted by light into a dimer not oxidized by permanganate and not capable of decolorizing bromine. Under analogous conditions, ethyl γ-ketopentadienedicarboxylate appears to suffer deep oxidative fission.

Exposure of an alcoholic solution of the yellow form of 2-hydroxystyrylmethyl ketone to rays of short wave-length from a quartz mercury vapor lamp for 24 hours produces a complete transformation to the colorless form.[168]

Derivatives of benzoylethylene also exhibit geometrical isomerizations. *Trans*-α,β-*bis*(2,4-dimethylbenzoyl)ethylene, on exposure to light, becomes coated with the *cis* isomer, which appears to revert slowly to the *trans* form on recrystallization.[169] α-Chlorodibenzoylethylene is transformed into the β-isomer by exposing a chloroform solution containing a trace of dibenzoyl-α,β-dichloroethane to strong sunlight for two hours. Dibenzoylbromoethylene is not, however, changed by sunlight. Dibenzoyldichloroethylene exists in two forms: α, melting at 63-65°C. is more soluble in chloroform than the β-form, melting at 162°C. The former is transformed into the latter by strong sunlight. Similar transformation occurs also in the case of the dibromo-derivative.[170] Sunlight also isomerizes the yellow benzoylethylene phenyl sulfone, as well as β-bromo-β-benzoylvinyl phenyl sulfone, to colorless isomers with altered melting points.[171]

Von Halban and Geigel[172] have shown that, in the case of tetrabenzoylethylene, an irreversible chemical change rapidly follows a primary phototropic process. Von Halban and Rast[173] state that when it is dissolved in acetic acid, concentrated sulfuric acid or sodium ethylate, a monohydrate can be crystallized out. On fur-

[159] Williams, D. M., *J. Chem. Soc.*, 1383 (1929).
[160] Stoermer, R., *Ber.*, **42**, 4865 (1909); **44**, 637 (1911); *J. Chem. Soc.*, **98**, II, 114 (1910)
[161] Vaidya, B. M., *Proc. Roy. Soc.*, **A129**, 299 (1930).
[162] Dey, B. B., Rao, R. H. R., and Seshadri, T. R., *J. Indian Chem. Soc.*, **11**, 743 (1934); **12**, 140 (1935); *Chem. Abs.*, **29**, 4752 (1935).
[163] Smakula, A., *Angew. Chem.*, **47**, 777 (1934).
[164] Stobbe, H., *Ber.*, **47**, 2701 (1914).
[165] Taylor, H. S., and Vernon, A. A., *J. Am. Chem. Soc.*, **53**, 2527 (1931).
[166] Dann, A. T., Howard, A., and Davies, W., *J. Chem. Soc.*, 607 (1928).
[167] Stobbe, H., Färber, E., and Rau, F., *Ber.*, **58B**, 1548 (1925).
[168] McGookin, A., and Heilbron, I. M., *J. Chem. Soc.*, **125**, 2102 (1924).
[169] Coulson, E. A., *J. Chem. Soc.*, 1406 (1934).
[170] Conant, J. B., and Lutz, R. E., *J. Am. Chem. Soc.*, **47**, 881 (1925).
[171] Kohler, E. P., and Larsen, R. G., *J. Am. Chem. Soc.*, **57**, 1448 (1935).
[172] von Halban, H., and Geigel, H., *Z. physik. Chem.*, **96**, 233 (1920).
[173] von Halban, H., and Rast, K., *Z. physik. Chem., Bodenstein-Festband*, 303 (1931).

Reimer [187] discussed the difference in behavior of the benzalpyruvates and the benzoylacrylic acids just described.

$C_6H_5CH{=}CHCOCOOR$ — *Benzalpyruvates*

$C_6H_5COCH{=}CHCOOR$ — *Benzoylacrylates*

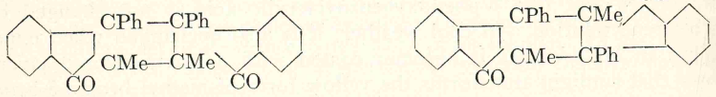
The system of conjugated double bonds is the same in each case, but its relation to the phenyl and carboxyl groups differs. The representatives of the first polymerize but those of the second isomerize instead. Miss Reimer later found [188] that benzalpyruvic acids in which methoxyl groups are substituted in the nucleus are less affected by sunlight. The most active substance is colorless β-bromobenzalpyruvic acid.[189] Its benzene solutions become lemon-yellow in two or three days in diffused light. Direct sunlight fades this to colorless, the color reappearing after removal from sunlight. The color change can be repeated many times and is remarkably sensitive to changes in intensity. From the decolorized solutions, a white crystalline dimer was isolated. It became brilliantly yellow overnight. The yellow form is regarded as a geometrical isomer of the original acid.

In stoppered tubes, there is also a photodecomposition of some of the compounds producing hydrogen bromide. The yellow form and the polymer are not obtained, but brown decomposition products result. Exposure of the original acid without a solvent yields slowly, without the formation of a colored intermediate, a crystalline dimer isomeric with that formed in benzene solution.

In the presence of oxygen, the benzene solution forms, in addition to the dimer, a bromoacid, apparently by the addition of the elements of hypobromous acid to the original unsaturated acid. When the benzene contains moisture, colorless crystals of a saturated, bromine-free acid, $C_{10}H_{10}O_6$, are also formed by photochemical "hydroxylation" at the double bond.

The polymerization products are cyclobutane derivatives. Ellingboe and Fuson [190] found that ultraviolet light has little or no effect on *trans*-1,2-dibenzoylcyclobutane in benzene. According to Vorländer and Daehn [191] 7-phenylheptatrienic acid and its sodium salt in aqueous suspension are strikingly stable, ultraviolet light decomposing only a small portion.

In benzene solution,[192] 3-phenyl-2-methylindone gives rise to two diphenyldimethyltruxones, one being white and melting at 307-308°C. and the other pale canary-yellow, melting at 259-260°C.



These compounds react with concentrated sulfuric acid to form 3-phenyl-2-methylindone. When the latter is exposed in benzene solution to the action of ordinary

[187] Reimer, M., *J. Am. Chem. Soc.*, **46**, 783 (1924).

[188] Reimer, M., and Kamerling, H. H., *J. Am. Chem. Soc.*, **55**, 4643 (1933); Reimer, M., Tobin, E., and Schaffner, M., *Ibid.*, **57**, 211 (1935).

[189] Reimer, M., *J. Am. Chem. Soc.*, **58**, 1108 (1936).

[190] Ellingboe, E., and Fuson, R. C., *J. Am. Chem. Soc.*, **56**, 1774 (1934).

[191] Vorländer, D., and Daehn, E., *Ber.*, **62B**, 545 (1929).

[192] DeFazi, R., *Gazz. chim. ital.*, **54**, 85, 1000 (1924); **57**, 551 (1927).

sunlight, the truxone melting at 307-8°C. is formed, together with what appeared to be a third isomer, yellow crystals of melting point 174-176°C. A third diphenyltruxone, $C_{30}H_{20}O_2$, yellow needles, m.p. 184-5°C., is obtained when the colorless isomers formed by treating ethyl β,β-diphenyl-lactate with concentrated sulfuric acid are exposed in benzene solution to ultraviolet rays. Ethylphenylindone does not give truxones when irradiated. Prolonged action of ultraviolet light on the 307-8°C. isomer of dimethyldiphenyltruxone in benzene converts it into methylphenylindone.

Bodforss [193] found that benzoylphenylethylene oxide, benzoyl-*m*-nitrophenylethylene oxide, and benzoyl-*p*-chlorophenylethylene oxide undergo rearrangement into phenyl α-hydroxystyryl ketones with increasing readiness when their solutions in methyl alcohol are exposed to a mercury lamp. The yields of the isomers are very small, but their presence can be demonstrated by the ferric chloride test for enols and by the precipitation of copper salts, from which they can be isolated.

Some of these transformations are phototropic, that is, the changes produced by light are reversed in darkness. This is notably the case with the fulgides studied particularly by Stobbe.[194] These are aryl derivatives of butadienedicarboxylic acid. Triphenylfulgide forms orange-red crystals which become dark brown in sunlight or in the rays of an arc lamp and which revert to their original color in darkness. The brown and orange forms seemed to be chemically identical. If the phototropic change is frequently repeated, the difference between the shades of the two forms becomes gradually less, a chemical change taking place which leads finally to the conversion of the fulgide into a new substance, the photoanhydride.

Phototropic change in these compounds was observed only in the case of the lemon-yellow to orange-red diaryl and the orange-red to dark red triarylfulgides; the colorless alphyl, greenish-yellow to yellow monoaryl and red, purple-red or brown or tetraarylfulgides are not phototropic. The modifications of a phototropic substance can exist in the pure state only during exposure to the wave-length of light which forms them since they revert in darkness to a mixture or solid solution of more than one form. The equilibrium between the two modifications in a mixture depends on the wave-lengths of light (and their relative intensities) to which it is exposed.

The phototropy of other substances than the fulgides has also been studied by Stobbe.[195] Red and blue rays have no action in reversing the color change produced by ultraviolet light on colorless β-tetrachloro-α-ketonaphthalene, only yellowish-green and yellowish rays being effective. A complete discussion of the many instances of phototropy would consume much space.[196]

Stereoisomerism of Oximes

Stereoisomeric changes about the carbon-nitrogen double bond in the benzaldoximes also occur. Ciamician and Silber [197] showed the nitrobenz-*syn*-aldoximes to be changed to the *anti* form when their benzene solutions were exposed in glass tubes to sunlight. (It must be noted that these and other workers used the configurations in the sense opposite to that at present accepted. Thus, they stated

[193] Bodforss, S., *Ber.*, **51**, 214 (1918); *Chem. Abs.*, **12**, 2554 (1918); *J. Chem. Soc.*, **114**, I, 232.

[194] Stobbe, H., *Annalen*, **359**, 1 (1908); *J. Chem. Soc.*, **94**, II, 339 (1908).

[195] Stobbe, H., *Ber. Verhandl. Sächs. Akad. Wiss. Leipzig*, **74**, 161 (1922); *Chem. Abs.*, **17**, 3020 (1923).

[196] For details, consult the review articles cited in Chapter 16. For benzylidene-, anisylidene- and cuminylidenehydrazones, see Biltz, H., and Wienands, A., *Annalen*, **308**, 1 (1899); *J. Chem. Soc.*, **76**, 910 (1899); tetraphenyldihydrotriazine, v. Walther, R., *J. Chem. Soc.*, **84**, i, 582 (1903); ethyl oxalisobutyrate, Wislicenus, W., and Kiesewetter, M., *J. Chem. Soc.*, **74**, i, 240 (1898); α-azoxynaphthalene, Cumming, W. M., and Steel, J. K., *J. Chem. Soc.*, **123**, 2464 (1923); tetrabenzoylethylene, von Halban, H., and Geigel, H., *Z. physik. Chem.*, **96**, 233 (1920); aminoaryldisulfoxides, Child, R., and Smiles, S., *J. Chem. Soc.*, 2696 (**1926**); diphenylacyldiphenylmethane, de Carvalho, A. P., *Compt. rend.*, **200**, 60 (1935). For further data on the fulgides, see Dietzel, R., and Naton, J., *Ber.*, **58B**, 1314 (1925); Stobbe, H., Ljungren, G., and Freyberg, J., *Ber.*, **59B**, 265 (1926); α-γ-diphenylallyl ether, Shoppee, C. W., *J. Chem. Soc.*, 2567 (**1928**). For "reversed phototropy," see Heilbron, I. M., and Wilson F. J., *J. Chem. Soc.*, **105**, 2892 (1914) and Heilbron, I. M., Hudson, H. E., and Huish, D. M., *ibid.*, **123**, 2273 (1923).

[197] Ciamician, G., and Silber, P., *Ber.*, **36**, 4268 (1903).

that the *anti* forms were converted to the *syn* forms.) Ciusa[198] reported similar changes in the case of *p*-chloro- and 3-nitro-*o*-methoxybenz-*syn*-aldoximes. He was unable to observe the conversion in the case of unsubstituted benz-*syn*-aldoxime or of 3,4-methylenedioxy-*syn*-aldoxime, and inferred that the presence of a negative substituent is necessary for the change to occur. By the use of a quartz mercury arc, however, Brady and McHugh[199] showed that this is not the case and that the conversions can be effected. The change occurred in all but two of a series of 24 aldoximes and their derivatives. 3,4-Dimethoxybenz-*syn*-aldoxime underwent no change[200] and 5-bromo-3,4-dimethoxybenz-*syn*-aldoxime suffered demethylation to 5-bromo-3-methoxy-4-hydroxybenz-*syn*-aldoxime. The methyl ether of benzaldoxime is decomposed by ultraviolet with the formation of benzonitrile, but the methyl ether of *m*-nitrobenzaldoxime undergoes no change. The methyl ethers of *m*- and *p*-nitrobenz-*syn*-aldoximes are partially isomerized, confirming earlier results obtained with sunlight,[201] but not so rapidly or completely as in the case of the oximes themselves. In subsequent work, Brady and Klein[202] succeeded in effecting the conversion in the α-*O*-*p*-nitrobenzyl ethers of *o*-, *m*- and *p*-aldoximes, of 3,4-methylenedioxybenzaldoxime, of *o*- and *p*-methoxybenzaldoxime, of 3-nitro-4-methoxybenzaldoxime, and of 5-nitro-2-methoxybenzaldoxime, as well as in α-*O*-methyl-6-nitro-3,4-methylenedioxbenzaldoxime. Although similar treatment of the α-*O*-methyl-3-nitro-4-methoxybenzaldoxime resulted in partial inversion, the product could not be separated into its components. Brady and Peakin[203] found that, apart from slight but profound decomposition, *m*-nitrobenzodimethylamidoxime is unchanged by exposure, in benzene solution in a silica vessel for 48 hours to the light of a quartz mercury lamp.[204]

The isomeric changes of the semicarbazones, particularly of cinnamaldehyde, have been discussed in previous paragraphs and it has been pointed out that some workers believe the changes can be attributed to tautomerism within the urea portion of the molecule without the necessity of considering stereoisomerism about the double bonds in other portions of the molecule. On exposing solutions of the semicarbazones of dypnone and phenyl-β-phenylstyryl ketone, and the mesityl oxide-δ-phenylsemicarbazones to a quartz mercury lamp, Wilson and Macaulay[205] observed that stereoisomers are formed. Attempts to prepare stereoisomers of the semicarbazones of benzylacetone, benzylacetophenone, methyl styryl ketone and styrylisobutenyl ketone gave negative results.

Phototropy is observed in many semicarbazones. Gheorghiu and Arwentiew[206] find the semicarbazone resulting from the condensation of methyl isobutyl ketone with anisaldehyde to become colored in diffused light, a general property of the semicarbazones of the aldehyde condensation products with ketones in the α- but not in the γ-position. Although the semicarbazones of ethylenic ketones of the type ArCH=CHCOR, in which Ar is aryl and R either alkyl or aryl, resulting from the alkaline condensation of methyl ketones with aromatic aldehydes are phototropic, those of the ketones ArCH=CRCOCH$_3$

[198] Ciusa, R., *Atti R. Accad. Lincei*, **15**, ii, 721 (1906).

[199] Brady, O. L., and McHugh, G. P., *J. Chem. Soc.*, **125**, 547 (1924).

[200] See Brady, O. L., and Dunn, F. P., *J. Chem. Soc.*, **123**, 1790 (1923).

[201] Brady, O. L., and Dunn, F. P., *J. Chem. Soc.*, **103**, 1624 (1913).

[202] Brady, O. L., and Klein, L., *J. Chem. Soc.*, 874 **(1927)**.

[203] Brady, O. L., and Peakin, F. H., *J. Chem. Soc.*, 2269 **(1929)**.

[204] For absorption data on various oximes and semicarbazones, see Ramart-Lucas, Mme., and Grumez, M., *Bull. soc. chim.*, **53**, 753 (1933); Ramart-Lucas, Mme., and Bruzau, Mme., *Bull. soc. chim.*, **11** 119 (1934). For thiocyanoacetoneoxime, Ponomarev, F. G., Alpatov, D. M., and Strepetov, N. P., Acta Univ. Voronegiensis, **9**, No. 3, 132 (1937); *Chem. Abs.*, **32**, 7021 (1938).

[205] Wilson, F. J., and Macaulay, R. M., *J. Chem. Soc.*, **125**, 841 (1924).

[206] Gheorghiu, C. V., and Arwentiew, B., *Ann. sci. Univ. Jassy*, **16**, 536 (1931); *Chem. Abs.*, **26**, 4804 (1932); see also Dickinson, R., Heilbron, I. M., and Irving, F., *J. Chem. Soc.*, 1888 **(1927)**.

obtained by acid condensation are stable to light.[207] Since the phototropy is connected with the presence of double bonds conjugated with the benzene nucleus, all changes disturbing the conjugation tend to diminish or eliminate the phenomenon. It is probable that the phototropic change consists in a shift of the valence electrons brought about by the action of light.

The thiosemicarbazones and δ-phenylsemicarbazones of the ethylenic ketones of the type ArCH=CHCOR are always phototropic.[208]

Aromatic Amines

The spectrum of aniline vapor includes 185 lines and bands between 1980 and 2632A and a continuous zone from 2632A.[209] Savard found for the excitation energies of three electronic states 97.9, 99.2 and 102 kcal. The energy of dissociation into C_6H_5NH and a hydrogen atom is 108 kcal.[210]

By studying the change in the ultraviolet absorption of solutions with change in pH, Hammett, Dingwall and Flexser[211] determined its dissociation constant. The well-known photochemical discoloration of aniline[212] is believed to be an oxidation. It is furthered by the presence of *o*- and *p*-phenylenediamine as impurities, but is retarded by the *m*-isomer and is almost completely inhibited in the absence of oxygen. It is also retarded by minute amounts of sodium sulfide or oxalic acid, or by contact with emery-surfaced zinc or iron plates, either untreated or previously boiled with 20-per cent sodium sulfide. On the other hand, if iron plates are cleaned by heating with dilute sulfuric acid, they accelerate the reaction even though they have been treated with sodium sulfide. Mild heating over a gas flame somewhat restores the preserving action. Partially rusted iron plates after boiling with 20-per cent sodium sulfide also retard the oxidation. These experiments were conducted to develop methods for the storage and transportation of aniline in iron drums. In the method recommended, the drums were flushed with hot water, and without further cleaning were boiled with 5- to 20-per cent sodium sulfide, sealed, allowed to cool, emptied, flushed with water and then twice with aniline and filled as soon as possible to avoid oxidation of the iron sulfide film. Yamanaka[213] believes light of the range 5100 to 3000A, and especially 4957 to 4300A to be most effective in producing the color. On the other hand, Freytag,[214] by exposing strips of hardened filter paper impregnated with aqueous or alcoholic solutions of 18 primary amines behind a quartz spectrograph, found the majority of them to be sensitive only to ultraviolet light of wave-lengths less than 3130A. The intensity of the color developed varied greatly with the wave-length employed. He finds[215] ultraviolet to markedly accelerate aniline black dyeing. Photographic negatives may be printed on cotton fabric impregnated with a 1- to 25-per cent solution of aniline hydrochloride containing five drops of potassium ferricyanide and 18 to 24 drops of 10-per cent aqueous potassium chlorate solution per 30 cc.,

[207] Gheorghiu, C. V., *Bull. soc. chim.*, **53**, 1441 (1933).

[208] Gheorghiu, C. V., *Bull. soc. chim.*, **1**, 97 (1934).

[209] Savard, J., *Compt. rend.*, **190**, 678 (1930); *Bull. soc. chim.*, **53**, 1404 (1933).

[210] See also, Horio, M., *J. Soc. Chem. Ind. Japan*, **37**, Suppl. 284 (1934). For a comparison of the spectra of aniline and acetanilide, see Klingstedt, F. W., *Z. physik. Chem.*, **1B**, 74 (1928). Benzylamine, Ley, H., and Volbert, F., *Ber.*, **59B**, 2119 (1926). Nitrosodimethylaniline, Custers, J. F. H., and Dippel, C. J., *Z. Physik*, **86**, 516 (1933). Nitroanilines, Glotz, G., *Bull. soc. chim.*, **1**, 1148 (1934). Toluidines, Morton, R. A., and McGookin, A., *J. Chem. Soc.*, 901 **(1934)**. Arylamines, Ramart-Lucas, Mme., and Wohl, Mlle., *Compt. rend.*, **196**, 1804 (1933). For fluorescence studies on amines, see Lumière, A., Lumière, L., and Seyewetz, A., *Bull. soc. chim.*, **37**, 700 (1925).

[211] Hammett, L. P., Dingwall, A., and Flexser, L., *J. Am. Chem. Soc.*, **56**, 2010 (1934).

[212] Bulich, P. K., *Anilinokrasochnaya Prom.* **3**, 405 (1933); *Chem. Abs.*, **28**, 1335 (1934).

[213] Yamanaka, T., *Bull Inst. Phys-Chem. Research (Tokyo)*, **14**, 396 (1935); *Chem. Abs.*, **30**, 1754 (1936).

[214] Freytag, H., *Z. wiss. Phot.*, **33**, 33 (1934); *Brit. Chem. Abs.*, **1934A**, 740.

[215] Freytag, H., *Melliand. Textilber.*, **13**, 144 (1932); *Chem. Abs.*, **27**, 1834 (1933).

exposing for fifteen minutes to ultraviolet light and washing away the unchanged aniline with water.

The reactions between aniline and nitrobenzene which occur during a five months' exposure to summer sunlight in sealed tubes have been studied by Vecchiotti and Piccinini.[216] The liquid became red-brown but was neutral in reaction and evolved no gas. Among the compounds identified were, besides unchanged nitrobenzene and resin, *o*-hydroxyazobenzene, azoxybenzene and a small quantity of *p*-aminophenol. The results are explained by regarding the initial reaction as a simultaneous oxidation and reduction of nitrobenzene forming nitrosobenzene and phenylhydroxylamine. The nitrosobenzene reacts with the phenylhydroxylamine to yield water and azoxybenzene, the latter then transforming into *o*-hydroxyazobenzene. The great tendency of phenylhydroxylamine to change to *p*-aminophenol accounts for the presence of this material. Decomposition products of nitrosobenzene probably enter into other secondary reactions.

In the reaction between toluene and nitrobenzene there were obtained,[217] in addition to benzoic acid and *p*-aminophenol, aniline and azoxybenzene. The benzoic acid is formed by oxidation of toluene by nitrobenzene which is reduced to nitrosobenzene. A molecule of unaltered nitrobenzene reacts with three of benzaldehyde, an intermediate oxidation product, to produce two of benzoic acid and one of benzoylaniline. The latter is then hydrolyzed to aniline and benzoic acid. Benzoylaniline also may be formed along with benzoic acid by the interaction of nitrosobenzene with two molecules of benzaldehyde.[218] Azoxybenzene may be formed either by the interaction of nitrosobenzene and benzaldehyde or, by analogy with the reaction of nitrosobenzene and phenylhydroxylamine, by the interaction of nitrosobenzene and benzoylphenylhydroxylamine. It might also be produced by a reaction between nitrosobenzene and *p*-$OHC_6H_4NHCOC_6H_5$. The compounds required for the last two processes were not isolated although their formation is conceivable. According to Knipscheer,[219] *o*-hydroxyazobenzene is formed by the action of light on azoxybenzene, but it was not identified by the Italian observers. The aniline is partly oxidized to phenylhydroxylamine, which under the influence of light, forms *p*-aminophenol.

The action of sunlight for six months on a mixture of *o*-nitrotoluene and aniline gave a product containing *p*-aminophenol, 2′-methylazoxybenzene, and an isomer of the latter, probably a benzeneazocresol.[220]

Plisov [221] made some preliminary experiments on the photochemical formation of salts of aromatic amines with alkyl halides in an attempt to determine whether the activation of the amine or of the halide is the determining factor in the reaction. Photochemical action is more evident in the combination of aniline with benzyl chloride than in the case of *o*-toluidine and benzyl chloride. In the former case, the yield in three hours increased from 15 per cent in darkness to 82 per cent under irradiation in a quartz vessel by an arc.

Migrations in N-Substituted Amines. Blanksma [222] has noted that acetylchloroaminobenzene is altered by light, following the general rule that the radicals

[216] Vecchiotti, L., and Piccinini, C., *Gazz. chim. ital.*, **61**, 626 (1931).
[217] Vecchiotti, L., and Zanetti, G., *Gazz. chim. ital.*, **61**, 798 (1931).
[218] Bamberger, E., *Ber.*, **35**, 1606 (1902); Ciamician, G., and Silber, P., *Atti accad. Lincei*, **14**, 265 (1905).
[219] Knipscheer, H. M., *Rec. trav. chim.*, **22**, 1 (1903).
[220] Vecchiotti, L., and Piccinini, C., *Gazz. chim. ital.*, **63**, 112, 319 (1933); *Brit. Chem. Abs., A*, 602 (1934).
[221] Plisov, A. K., *Gazz. chim. ital.*, **59**, 200 (1929); *Chem. Abs.*, **23**, 4198 (1929).
[222] Blanksma, J. J., *Proc. K. Akad. Wetensch. Amsterdam*, **5**, 178 (1902); *J. Chem. Soc.*, **82**, II, 646 (1902).

Br, Cl, NO_2, NO and O, attached to nitrogen, change places, under the influence of sunlight, with a hydrogen atom in the nucleus. Chattaway and Orton also made some velocity measurements on the transformation of the compound in sunlight,[223] and had previously studied the thermal reaction for which Armstrong [224] found a trace of hydrogen chloride essential. Mathews and Williamson [225] have studied the reaction in solutions in benzene, alcohol and acetic acid, using a quartz mercury lamp. The solvent exerts a marked effect, but hydrochloric acid is not required for the photoreaction. The addition of water to an alcoholic or glacial acetic acid solution greatly diminishes the velocity of the photo-decomposition. In the absence of water, the reaction in these solvents proceeds without the action of radiation, after having been started in this manner. In the presence of water, this effect is lacking and the reaction is truly photochemical.

Porter and Wilbur,[226] who presented data on the absorption of ultraviolet by acetylchloroaminobenzene and its rearrangement product, found the transformation to occur in the solid phase as well as in solution. Hodges [227] found the rate of the change under the influence of the 3569A line in eight solvents very slow in the complete absence of water. It is a chain reaction, the quantum yields being 5-6 in carbon tetrachloride, 15-18 in bromobenzene, 17 in chloroform, 22 in chlorobenzene, 29-33 in benzene, 108-116 in toluene, 156-163 in cyclohexane, and 188 in decalin. In closely related solvents, the reaction velocity diminished with increasing dielectric constant, surface tension and density.

Condensation Reactions of Amines. The condensation of *p*-phenetidine hydrochloride with epichlorohydrin to N,N-*bis*(γ-chloro-β-hydroxypropyl)-*p*-phenetidine is accelerated by sunlight.[228]

Qualitative observations on the nature of the products formed by the prolonged exposure to tropical sunlight of a number of organic compounds in 2 per cent solutions in water, dilute acid or alkali or alcohol have been recently reported by Malaviya and Dutt.[229] Aniline in hydrochloric acid precipitated phenazine in 135 days, *o*-toluidine gave 1,5-dimethylphenazine, *m*-toluidine, 2,6-dimethylphenazine and *p*-toluidine probably gave 3,7-dimethylphenazine. Dimethylaniline did not change in 141 days and 1,3,4-xylidine gave only a trace of precipitate in 121 days.

α-Naphthylamine probably gave α,β-dinaphthazine and β-naphthylamine probably β,β-dinaphthazine. *o*-Nitraniline was unaffected. *p*-Nitrosodimethylaniline in aqueous solution was oxidized to *p*-nitrodimethylaniline, but in dilute acid, it gave an unidentified precipitate and benzidine gave an unidentified phenazine. In dilute acid, *o*-phenylenediamine gave 2,3-diaminophenazine hydrochloride, the *m*-compound 2,6-diaminophenazine and the *p*-compound probably 3,6-diaminophenazine. *p*-Aminodimethylaniline gave an intensely violet solution of an unidentified azine dye. Aqueous *p*-amino-acetanilide gave diacetyl-*p*,*p*′-diaminodiphenylamine. 1,8-Diaminonaphthalene gave a brown precipitate, probably *peri*-dinaphthalene azotide. *o*-Aminophenol formed a red compound, $C_{24}H_{19}N_3O_2$, the *m*-compound an unidentified brown precipitate, and the *p*-compound a violet precipitate, probably *p*,*p*′-dihydroxydianilinoindophenol. *m*- and *p*-Hydroxydimethylanilines were unaffected. 1,5-Dimethoxyphenazine was formed from *o*-methoxyaniline,

[223] Chattaway, F. D., and Orton, K. J. P., *Proc. Chem. Soc.*, **81**, 200 (1902).
[224] Armstrong, H. E., *J. Chem. Soc.*, **77**, 1047 (1900).
[225] Mathews, J. H., and Williamson, R., *J. Am. Chem. Soc.*, **45**, 2574 (1923).
[226] Porter, C. W., and Wilbur, P., *J. Am. Chem. Soc.*, **49**, 2145 (1927).
[227] Hodges, F. W., *J. Chem. Soc.*, 240 (1933).
[228] Strukov, I. T., *Khim. Farm. Prom.*, No. 2, 11 (1934); *Chem. Abs.*, **28**, 5421 (1934).
[229] Malaviya, B. K., and Dutt, S., *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 319 (1935); *Chem. Abs.*, **30**, 1056 (1936).

the 3,7-compound from the *p*-derivative and corresponding diethoxyphenazines were produced from the ethoxy-compounds. 2,4-Hydroxyphenylenediamine gave an unidentified phenazine. Aminobenzoic acid gave phenazine-1,5-dicarboxylic acid, the *m*-compound did not alter, but the *p*-acid in alkaline solution gave the sodium salt of *p,p'*-azobenzenedicarboxylic acid.

Vanillin, 2,4-dihydroxybenzaldehyde and *p*-dimethylaminobenzaldehyde were unchanged. Aqueous *p*-aminobenzaldehyde hydrochloride gave *p,p'*-dialdehydeazobenzene.

Aqueous 1-per cent eosin was decolorized in 75 days, giving hydrogen bromide and a precipitate of 2,4-dibromobenzoylbenzoic acid. Similarly erythrosine gave hydrogen iodide and probably 2,4-diiodobenzoylbenzoic acid. *p*-Aminoacetophenone gave an unidentified precipitate, capable of reducing ammoniacal silver nitrate, but gallacetophenone was unaffected. Phenylhydrazine evolved nitrogen and formed an unidentified, apparently heterocyclic nitrogen compound. 2-Aminothiazole gave a trace of a phenazine derivative. Aqueous thiocarbamide gave sulfur and carbamide in 46 days. α-Benzildioxime in dilute alkali gave 3,4-diphenylfurazan in 35 days.

Color Reactions of Amines. Schall [230] proposed to test for ultraviolet rays by their ability to form a blue coloration on filter paper impregnated with *p*-phenylenediamine nitrate (2/3*N*) and dried. Such paper is sensitive only to wave-lengths shorter than 3130A. Diffused daylight produces only a pale gray tint but a quartz mercury lamp produces a blue color in an instant. Mott and Bedford [231] made the paper by impregnating white blotting paper in a solution of 1 g. *p*-phenylenediamine, 3 cc. of water and 2 cc. of nitric acid, s.g. 1.21, and drying one-half hour in a steam oven.

Freytag [232] states also that irradiation of moist filter paper or cotton fabric impregnated with solution containing about 0.1 per cent of either phenylenediamine, or their mixtures, resulted in yellow to brown color formation due to oxidation of the base. This was assisted by the presence of 0.1 per cent sodium nitrate and potassium nitrate. The resulting colors were faster to washing when aniline was also present. The process could be adapted to the production of photographic prints on fabric.

Nile-blue, brilliant green, Capri-blue, phenosofranine, fuchsin and pinakryptol-green are negative catalysts toward the photochemical decomposition of "Aktivin," sodium *p*-toluenesulfonchloroamide, in methanol solution.[233] Malachite-green had no effect, and pinakryptol-yellow and methylene-blue were positive catalysts, even in darkness.

The photochemical oxidation of aqueous solutions of benzidine in the presence of eosin is accelerated by manganese salts and by iron and copper salts in decreasing quantities.[234] Eosin, chlorophyll and the fluorescent derivatives of the latter bring about the oxidation of benzidine in methanol. Green leaves in water solutions of benzidine also bring about its oxidation when illuminated.

Picric acid, in solutions at pH 13.0, is decomposed in ultraviolet light to give picramic and isopurpuric acids, nitrous acid, ammonia and hydrogen cyanide. The

[230] Schall, C., *Photograph. Wochenblatt*, **33**, 321 (1907); *Chem. Ztg.*, **34**, 267; *Z. physik. Chem. Unterr.*, **21**, 389 (1908).

[231] Mott, W. R., and Bedford, C. W., *J. Ind. Eng. Chem.*, **8**, 1029 (1916).

[232] Freytag, H., *Melliand. Textilber.*, **13**, 322 (1932); *Chem. Abs.*, **27**, 1834 (1933).

[233] Milbauer, J., *Phot. Korr.*, **71**, 94 (1935); *Brit. Chem. Abs.* **A**, 1468 (1935); *Chem. Listy*, **29**, 267 (1935); *Chem. Abs.*, **30**, 1661 (1930)

[234] Noack, K., *Phot. Korr.*, **62**, 73 (1926); *Chem. Abs.*, **21**, 1409 (1927).

usual yellow form present at lesser pH values is unaffected.[235] An analogous reaction occurs with 2,5-dinitrophenol. *o*- and *p*-Nitrophenols, 2,4- and 2,6-dinitrophenols and 2,4-dinitro-*o*-cresols decompose at reactions at which the red forms exist, the rate increasing with the pH. These darken with the formation of an amino- group.

Textiles of animal or vegetable fibers impregnated with nitrophenols, nitroamines, or even colorless nitro- compounds, turn brown when exposed to daylight or ultraviolet rays.[236] Reduction apparently takes place, as reducing agents hasten, and oxidizing agents retard, the effect. The brown substance thus formed from picric acid on calico was isolated, by extraction with alkali and precipitation with acid, and found to contain nitro- or nitroso- groups, but no amino- group. This substance may be an azo- compound derived from an azoxy-reduction product of picric acid.

Azo, Diazo and Related Compounds. Knipscheer [237] has shown that azoxybenzene is converted by light into *o*-hydroxyazobenzene. He obtained the latter in poor yield (10.3 per cent) and with much loss of material by volatilization (39.7 per cent) by exposing sheets of filter paper impregnated with azoxybenzene to sunlight for five weeks. Cumming and Ferrier,[238] who believed the loss by volatilization could be obviated by making the exposures in solution, employed a mercury vapor lamp as source. The best results (28.0 per cent) were obtained by 50 hours' exposure in absolute ethanol and the smallest (7.7 per cent) with benzene as solvent. Increase of temperature improved the yield only slightly, but materially increased the loss of azoxybenzene by volatilization. The transformation also takes place in sunlight, but cannot be effected by an ordinary electric light.

The action of light on the α-isomer of benzeneazoxy-*p*-toluene, $NC_6H_4O{=}N.C_6H_4CH_3$ yields a red substance, probably an *o*-hydroxy- compound.[239] The β-isomer, $NC_6H_4{=}NO.C_6H_4CH_3$, very slowly turns yellow.

Cumming and Ferrier also obtained hydroxyazo- compounds from 2,2'-, 3,3'- and 4,4'-azoxytoluenes, 4,4'-dichloroazoxybenzene and 2,2'-diamino-4,4'-azoxytoluene. 4,4'-Azoxyanisole, 4,4'-azoxyphenetole, and 4,4'-dinitroazoxybenzene reacted slightly or not at all. In the case of 2,2'-azoxytoluene, products of widely different melting points were obtained in alcohol and in benzene as solvents. The hydroxyazo- compounds were obtained as red needles of varying solubility in sodium hydroxide solution. In cases in which the orientation could be determined, the hydroxyl group appeared to enter the benzene nucleus in the ortho position with respect to the azo-group.[240]

The decomposition of a 0.4 per cent solution of diazosulfanilic acid in ultraviolet light is proportional to the time of irradiation until 90 per cent has been decomposed; the remainder condenses with the phenol produced.[241] At pH values less than 7, the diazo- solution is very sensitive to light, but relatively stable to heat, while in alkaline solutions, the reverse is true. Similar results are obtained at 35°, 56°, 80° and 100°C., but when the temperature approaches that at which thermal decomposition of the diazo- compound occurs, this action predominates. Substitution of negative

[235] Molnar, J., *Compt. rend.*, **201**, 1482 (1935).

[236] Seyewetz, A., and Mounier, D., *Compt. rend.*, **185**, 1279 (1927).

[237] Knipscheer, H. M., *Rec. trav. chim.*, **22**, 1 (1903).

[238] Cumming, W. M., and Ferrier, G. S., *J. Chem. Soc.*, **127**, 2374 (1925).

[239] Bigiavi, D., and Sabatelli, V., *Gazz. chim. ital.*, **57**, 557 (1927); *Chem. Abs.*, **22**, 395 (1928).

[240] See also Ramsperger, H. C., for some determination of reaction rates for the thermal and photochemical decomposition of azo- compounds, *Proc. Nat. Acad. Sci.*, **13**, 849 (1927).

[241] Seyewetz, A., and Mounier, D., *Compt. rend.*, **186**, 953 (1928); *Bull. soc. chim.*, **43**, 827 (1928); *Brit. Chem. Abs.*, **1928A**, **493**.

radicals in the benzene nucleus, which increases the stability of the diazo- compound to heat, decreases its stability to light, the order of increasing stability being *p*-OH (anhydride) < *p*-SO_3H (anhydride) < *p*-COOH (anhydride) < *p*-Cl (chloride) < *p*-NO_2 (chloride) < benzenediazonium chloride. Decomposition is complete only in the first two cases. The effect of the nitro- group is the same in the ortho, meta and para positions. Decomposition by light of the diazo- compounds derived from sulfanilic acid, *p*-aminophenol, and aniline yields the corresponding phenol as in thermal decomposition; the derivative of *p*-aminobenzoic acid yields *p*-hydroxy- and *p*-chlorobenzoic acids, while from the brown precipitate obtained by decomposition of nitrobenzenediazonium chlorides is isolated a substance which is probably dinitrodiphenyl ether.

By comparing the absorption spectra before and after photolysis, Fukushima and Horio [242] concluded that the photodecomposition of diazobenzene sulfonic acid differs from the thermal reaction. It is effected by radiations of wave-length shorter than 3800A. The reaction is of zero order. An inner filter, such as quinine sulfate, retards the photolysis. The effects of temperature are complex.

Azo compounds may be photosensitized by zinc oxide, according to Fukushima, Horio and Omori.[243] In dilute alcoholic solution and an oxygen-free atmosphere in the presence of zinc oxide, azobenzene was reduced almost quantitatively to hydrazobenzene, but with pure oxygen there was no reduction in six months.[244]

Lyashenko and Kirzner [245] carried out the photolysis of phenyldiazonium chloride and its *o*-, *m*-, and *p*-substituted derivatives under exactly similar conditions by exposing the diazo- solutions for three hours to the action of daylight and the light of a mercury vapor lamp. The nitrogen eliminated was measured. They found that substitution in the meta position either increases the stability of aniline to light or has no influence. Substitution in the ortho and para positions decreases it. The ethoxy- group in the para position has no effect.

Other Compounds. The condensation products of aromatic thiohydrazide with aldehydes, ketones, and sugars on irradiation with the lines 6250, 5950 and 5430A exhibit a rapid drop of the rotatory power from a high value in one direction through zero to a maximum in the opposite direction.[246] Continued exposure causes the rotation again to reach zero and then to attain a maximum in the initial direction, after which it slowly drops off to zero. This is explained as a combination of partial racemization, *cis-trans* isomerization and a change in structure, all of which are affected by light.

2,2′-dinitro-5,5′-dimethoxydiphenyl disulfide rapidly turns yellow in sunlight.[247]

[242] Fukushima, I., and Horio, M., *J. Soc. Chem. Ind. Japan*, **34**, *Suppl. binding*, 367, 372, 374 (1931); *Chem. Abs.*, **26**, 2377 (1932).

[243] Fukushima, I., Horio, M., and Omori, M., *J. Soc. Chem. Ind. Japan*, **35**, *Suppl. binding*, 398 (1932); *Chem. Abs.*, **26**, 5848 (1932).

[244] The formation of equilibrium between *cis* and *trans* forms of azobenzene can be activated by light. Hartley, G. S., *Nature*, **140**, 281 (1937); von Auwers, K., *Ber.*, **71B**, 611 (1938); Cook, A. H., *J. Chem. Soc.*, 876 (1938).

[245] Lyashenko, V. D., and Kirzner, N. A., *Anilinokrasochnaya Prom.*, **4**, 272 (1934); *Chem. Abs.*, **28**, 7164 (1934).

[246] Lifschitz, I., and Froentjes, W., *Rec. trav. chim.*, **55**, 753 (1936).

[247] Hodgson, H. H., and Handley, F. W., *J. Chem. Soc.*, 542 (1926).

Chapter 26

Compounds with Condensed Ring Systems

Naphthalene Derivatives

There appear to be no descriptions of photochemical reactions of naphthalene. However, its absorption spectrum and also spectra of many of its alpha- and beta-derivatives have been investigated by de Laszlo.[1] Its vapor exhibits about 400 sharp narrow bands with fine structure between 3200 and 2820A and a group of broad continuous bands without fine structure between 2820 and 2500A.

Although naphthalene vapors are stable to the light of the quartz mercury arc, 1,2- and 1,4-dihydronaphthalenes quickly decompose to naphthalene. Tetralin decomposes more slowly, forming unidentified polymerization products.[2]

A number of nitro- derivatives of naphthalene are light-sensitive, producing brown colors which result from the reduction of nitro- groups. Much work has been devoted to the study of the mutual effects of nitro- and sulfonic acid groups in various positions upon the light sensitivity. One of the earliest instances observed was that in which yellow dyeings on wool of 1,6,4,8-diaminonaphthalenedisulfonic acid became brown rapidly on insolation.[3] The mono-nitro-derivatives of α- and β-naphthalenesulfonic acid are equally sensitive, but 2,4,8-dinitronaphthalenesulfonic acid is fast to light. Since, however, 1,8-nitronaphthalenesulfonic acid is highly sensitive, although the 1,5- compound is not, and since the 1,6- and 1,7- compounds are nearly equally sensitive, the degree of sensitiveness appears to be related to the positions of the nitro- and sulfonic acid groups in the nucleus.

The nitrosulfonic acids are said also to be sensitized to light by the addition of aromatic amines, due to oxidation of the amines by the nitro- group. The corresponding sulfinic acids and sulfonamides also give light-sensitive dyeings.

In the benzene series,[4] the sensitiveness to light decreases in the order ortho, para and meta, while the sensitiveness of *o*-nitrobenzenesulfonic acid is equal to that of *o*-nitrobenzenedisulfide, although considerably less than that of 1,8-nitronaphthalenesulfonic acid. It was suggested that the sensitiveness to light is imparted by the sulfur molecule rather than by the sulfonic group as a whole. The sensitiveness of 1,2-nitronaphthalenesulphonic acid and its salts is but little less than that of the 1,8-compound. Substitution of the hydrogen atom in the sulfonic acid group does not affect the photochemical properties of the nitrosulfonic acids, but the close proximity of the nitro- and sulfonic acid groups in the same ring has a positive influence on it. The dark precipitate formed by irradiation of the 1,8-compound is probably 1-amino-8-(8-nitro-1-naphthylsulfonyl)-2-naphthol, or

[1] de Laszlo, H. G., *Compt. rend.*, **180**, 203 (1925); *Z. physik. Chem.*, **118**, 369 (1925); *Proc. Roy. Soc.*, **111A**, 355 (1926). See also Charlampowiczowna, B., and Marchlewski, L., *Bull intern. acad. Polonaise*, **A**, 376 (1930); Obreimov, I., and Prichotjko, A., *Physik, Z. Sowj.*, **1**, 203 (1932); Kimura, S., *Mem. Coll. Sci. Kyoto Imp. Univ.*, **14**, 303 (1931); *Chem. Abs.*, **26**, 1516 (1932).

[2] Kemula, W., and Dunicz, B. L., *Z. physik. Chem.*, **A181**, 359 (1938).

[3] Vorozhtzov, N. N., and Gribov, K. A., *J. Gen. Chem. (U.S.S.R.)*, **2**, 929 (1932); *Chem. Abs.*, **27**, 2440 (1933).

[4] Vorozhtzov, N. N., and Kozlov, V. V., *J. Gen. Chem. (U.S.S.R.)*, **2**, 939 (1932); **7**, 996, 1610 (1937); *Chem. Abs.*, **27**, 2440 (1933); **31**, 5349, 8528 (1937); *Org. Chem. Ind. (U.S.S.R.)*, **4**, 399 (1937).

an isomer containing another hydroxyl group and an NO instead of an NO_2 group. When the magnesium salt of 1,8-nitronaphthalenesulfonic acid is exposed to sunlight, the dark precipitate is probably the cyclic magnesium salt of 2-hydroxy-1,1′-azonaphthalene-8,8′-disulfonic acid.

The change occurs better on wool than on silk or cotton, but it can also be observed in aqueous solutions of the salts, especially the magnesium salt. The reaction is faster in neutral or alkaline than in acid solutions. It is hindered by oxidants. When the substituents are in the "quinogenic" (1,5 and 1,7) positions, the acid is less sensitive than when they are in the 1,6 and 1,8 positions. When paper soaked in these solutions and exposed to light is rinsed with dilute sodium bichromate solutions, the colors are set better than if pure water is used. Nitroanthracene-1-sulfonic acid forms a dark compound when exposed to light, but *meso*-nitro-anthracene-2-sulfonic acid gives a colorless compound.

Steiger [5] studied a number of these compounds, as well as some containing the nitro- group and, in place of or in addition to the sulfonic acid group, the methyl group. The 1,8-nitromethylnaphthalene is more sensitive than *o*-nitrotoluene and nitronaphthalene. Its 5-sulfonic acid also is extremely sensitive. Pyridinium 1-nitronaphthalene-8-sulfonate and the corresponding N-methylpyridinium salt, like potassium 1-nitronaphthalene-8-sulfonate, are also very sensitive. Compounds of the series $5,1,8\text{-}C_{10}H_5(NO_2)SO_2X$ with a substituent in position 5 are more sensitive than those without it. The sensitivity varies with the group X and with the solvent employed.

Data for the absorption of twenty substituted 1,2- and 1,4-naphthaquinones have been given by Beck, MacBeth and Winzor.[6] These observations played a part in the determination of the structures of two dyes, droserone and hydroxydroserone, derived from the insectivorous plant, *Drosera whittakeri*.

The substituted naphthoquinone, 2-methyl-1,4-naphthaquinone, gradually loses its color in sunlight.[7] After two months, ether removed a colorless irradiation product, melting at 235°C. It is a dimer formed by 3,4-addition of two molecules of the naphthaquinone and contains a cyclobutane ring. That the quinone carbonyl groups did not function in the dimerization was shown by the formation of a tetraoxime of the dimer. These observations were made in the course of an investigation of the structure of the pigment phthiocol of the tubercle bacillus.

Dilute aqueous solutions of 2-hydroxy-1,4-naphthaquinone at 70°C. on exposure to ultraviolet light give isonaphthazarin and mainly, 3,3′-dihydroxy-2,2′-dinaphthyl-1,4,1′,4′-diquinone.[8]

When the reaction product of 3-chloro- or 3-bromo-1,2-naphthoquinone and 2,3-dimethylbutadiene in chloroform is heated at 100°C. in sunlight, the red solution becomes yellow in about 45 minutes, then changes to red and finally becomes yellow again. After five hours there results 36 per cent of 2,3-dimethyl-1,4,11,12-tetrahydrophenanthrenequinone-11,12-*endo*-2′,3′-dimethyl-2′-butene. In the dark, 16 to 20 hours of heating would be required. The product is a brilliant yellow, changing to nearly colorless on exposure to the light.[9]

An acid formed by the action of alkali and red mercuric oxide on 4-methyl-β-naphthopyrone followed by treatment with hydrochloric acid, when dissolved in

[5] Steiger, R. E., *Helv. Chim. Acta*, **16**, 793, 1315 (1933); **17**, 701, 1354 (1934).

[6] Beck, A. B., MacBeth, A. K., and Winzor, F. L., *Australian J. Exptl. Biol. Med. Sci.*, **12**, 203 (1934); *J. Chem. Soc.*, 325, 334 (1935).

[7] Madinaveitia, J., *Rev. acad. cienc. Madrid*, **31**, 617 (1934); *Chem. Abs.*, **29**, 5438 (1935); *Anales soc. espan. fis. quim.*, **31**, 750 (1933); *Chem. Abs.*, **28**, 1036 (1934).

[8] Hooker, S. C., *J. Am. Chem. Soc.*, **58**, 1212 (1936).

[9] Fieser, L. F., and Dunn, J. T., *J. Am. Chem. Soc.*, **59**, 1021 (1937).

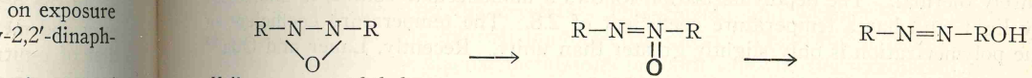
chloroform, is converted into 4-methyl-β-naphthopyrone to the extent of 70 per cent by the action of ultraviolet rays. On the other hand, a modification of the original acid, which melts at 146°C. rather than 112°C. and which is regarded as having the *cis* configuration, is unaltered when similarly treated.[10] It is suggested that the *trans* form is converted into the *cis* form during irradiation. The molecules of the latter may, however, be activated in such manner that the transformation does not stop at this stage, but proceeds further until cyclization to the stable coumarin-type of molecule has been effected. On the other hand, irradiation does not appear capable of activating the molecules of the *cis* form to the extent necessary for formation of the pyrone.

Aqueous solutions of sodium naphthionate undergo a change in surface tension in light. By placing a drop of the liquid in a horizontal capillary tube and exposing one meniscus to light from a mercury arc, Grumbach and Schlivitch [11] estimated the increase in surface tension by the speed of motion toward the lighted end. It is of the order of 1 to 2 mm. per hour. Aqueous solutions of fluorescein, sulfofluorene and uranyl nitrate, xylene solutions of anthracene and alcoholic solutions of xylene and gasoline behave in a similar manner but solutions of ferric chloride or oxalic acid do not.

The ammonium salt of α-nitrosonaphthylhydroxylamine reddens when applied to filter paper and exposed to the rays from a quartz mercury-vapor lamp. Rays of wave-lengths transmitted through glass are effective in producing this change.[12]

β,β-Azoxynaphthalene, which has a pure yellow color and melts at 164°C. on exposure to light (preferably in alcoholic solution) is converted irreversibly into a red isomer melting at 162°C. Both forms are stable toward alcohol in the dark.[13] The α,α′-azoxynaphthalene undergoes a change to a red form [14] regarded as a hydroxyazonaphthalene. Despite the fact that attempts to characterize the red modification as such by benzoylation or methylation failed, support for this structure is afforded by a comparison of the absorption spectra of both forms with that of β-naphthaleneazo-β-naphthol.

Cumming and Steel,[15] however, note that exposure of the α,α′-azoxynaphthalene to sunlight or to the light of a mercury-vapor lamp for a short period produced a red isomer of the same melting point. Further exposure produced an azonaphthol, melting at 224°. This change they formulate:



Yellow azoxynaphthalene — *Red isomer* — *Azonaphthol*

1,2,7,8-Di-(1′,5′-tetrazolo)-4-methyl-(1,8-naphthyridine, 1,2,7,8-tetrahydride), a light yellow material, becomes brown in a few days in air and light.[16]

Exposure to light converts β-2-hydroxy-1-naphthylcrotonic acid completely into 4-methyl-β-naphthopyrone, if sufficiently prolonged. β-Dimethylcoumaric acid yields 4,7-dimethylcoumarin.[17]

[10] Dey, B. B., and Lakshminarayanan, A. K., *J. Indian Chem. Soc.*, **11**, 373 (1934); *Chem. Abs.*, **28**, 6145 (1934).

[11] Grumbach, A., and Schlivitch, S., *Compt. rend.*, **181**, 241 (1925).

[12] Baudisch, O., and Fürst, R., *Ber.*, **45**, 3426 (1912).

[13] Cumming, W. M., and Ferrier, G. S., *J. Chem. Soc.*, **125**, 1108 (1924).

[14] Baudisch, O., and Fürst, R, *Ber.*, **45**, 3426 (1912).

[15] Cumming, W. M., and Steel, J. K., *J. Chem. Soc.*, **123**, 2465 (1923).

[16] Seide, O., *Ber.*, **59B**, 2465 (1926).

[17] Murty, K. S., Rao, P. S., and Seshadri, T. R., *Proc. Indian Acad. Sci.*, **6A**, 316 (1937); *Chem. Abs.*, **32**, 3362 (1938).

Anthracene

This hydrocarbon differs from naphthalene in exhibiting an interesting polymerization reaction. Anthracene exhibits strong absorption bands at 3800, 3600, 3400 and 3260A.[18] Bands were also found at 4450 and 4750A by Taylor and Lewis,[19] who believed absorption in these bands to be responsible for the occurence of the polymerization reaction. Subsequently, however, it was shown that the latter two bands are due to the presence of chrysogen as an impurity.[20] Capper and Marsh observed that pure white anthracene fluoresces with a violet-blue color, and that the addition of a trace of chrysogen changes this to the familiar magnificent green glow observed in most samples. For this reason, to excite the true fluorescence of anthracene the exciting light would have to be shorter than 4100A. They believed the light effective in polymerization must lie between the first absorption band at 3750A and 3100A since the reaction can be carried out in glass. Castille[21] finds anthracene to exhibit ten bands between 3800 and 2850A and two more in the extreme ultraviolet.[22]

The formation of an insoluble white precipitate when anthracene is irradiated in benzene solution and the recognition that it is dianthracene were subjects of early observations by Fritsche,[23] Elbs,[24] and Orndorff and Cameron.[25] In darkness the polymer yields anthracene by a thermal reaction which goes practically to completion. The process has been employed as a means for the purification of anthracene.[26] A solution of crude anthracene in benzene, toluene or coal-tar naphtha is irradiated by ultraviolet rays, the dianthracene separating and leaving carbazole, phenanthrene and most of the other compounds originally present as impurities in solution. The dianthracene is filtered off and reconverted into anthracene by sublimation, yielding a product of purity of 95 per cent or higher. The method has also been employed for the removal of anthracene from such materials as phenanthrene and fluorene in which it is a contaminant.[27]

The photostationary states set up between the polymerizing photochemical and the depolymerizing thermal reactions in phenetole, anisole and xylene solutions were studied by Luther and Weigert.[28] This is an instance of a photostationary state between two reactions one of which is purely photochemical and the other purely thermal. The depolymerization follows a unimolecular course, is unaffected by light, and has a temperature coefficient of 2.8. The temperature coefficient of the polymerization is only slightly greater than unity. Recently, Lauer and Oda[29] found the polymerization rate to be the same in hexane, cyclohexane, cyclohexene and ethanol. It is considerably greater in acetic acid and, particularly, in benzene. This is attributed to an effect of these solvents in displacing the absorption spectrum of anthracene toward longer wave-lengths. Double bonds in the solvent molecules have a distinct accelerating effect on the reaction. The results in cyclohexene were somewhat uncertain because of a darkening of the solvent. It was also found by Luther and Weigert that in solutions in which absorption was complete a further increase of anthracene concentration tended to increase the rate of polymerization, the rates approaching a limit at higher concentrations. Various early fruitless attempts were made to account for this.[30]

Recently, Weigert[31] verified the dependence of the rate upon concentrations in excess of those at which absorption is complete. He employed the lines 3660 and 3130A of the mercury arc. At very low concentrations, below 0.005 per cent, the yield was approximately proportional to the concentration. At higher ones, the rate increased with concentration approaching asymptotically a maximum at about 2 per cent concentration. Between 87° and 137°C., no influence of temperature or solvent was observed. The quantum yields were 0.254 at 3660A and 0.228 at 3130A.

Weigert proposed a more elaborate mechanism for the polymerization than that of Bodenstein who merely assumed that an activated anthracene molecule on collision with a normal one formed the polymer. Weigert assumed that an activated molecule on collision may utilize its activation energy in opening the bond between the two central carbon atoms forming a diradical with two tervalent carbon atoms. Two of these can then unite to produce the polymer.

There is the possibility that this mechanism is unnecessarily elaborate and that the diradical may be directly produced as a result of absorption. Clar[32] suggested that the origin of certain absorption bands is referable to the production of unpaired electrons at the meso- positions. Schönberg[33] assumes a photoequilibrium between the normal and the diradical forms of certain anthracenes, which cannot be magnetically detected because of the small concentration of the diradical form.

When anthracene is irradiated with short wave-lengths (1800 to 2000A), it exhibits a photoelectric effect.[34] At the same time there occurs a surface formation of dianthracene on the crystals. This Suzuki and Volmer[35] regard as an effect secondary to the internal photoelectric effect. They find it possible to prevent its formation by placing metal foils on both sides of the irradiated face and applying a field of 2000-14000 volts per cm.

Behavior of Various Anthracene Derivatives. Polymerization of β-methyl anthracene is a photochemical reaction similar to that of anthracene.[36] 2-3-Benzanthracene in xylene is readily oxidized by air to the quinone with the aid of ultraviolet light.[37] The oxidation of dihydrobenzanthrone is markedly accelerated by light.

[18] Hyatt, J. M., *Phys. Rev.*, **19,** 391 (1922).

[19] Taylor, H. A., and Lewis, W. C. M., *J. Am. Chem. Soc.*, **46,** 1606 (1924).

[20] Capper, N. S., and Marsh, J. K., *J. Am. Chem. Soc.*, **47,** 2847 (1925).

[21] Castille, A., *Bull. acad. roy. med. Belg.*, **8,** 74 (1928); see also Shishlovskiĭ, A. A., *Compt. rend. acad. sci. U.R.S.S.*, **15,** 29 (1937); *Chem. Abs.*, **31,** 6110 (1937).

[22] For further data on various derivatives, see Barnett, E., Cook, J. W., and Ellison, T. E., *J. Chem. Soc.*, 885 (**1928**); Pestemer, M., and Cecelsky, J., *Monatsh.*, **59,** 113 (1932); Clar, E., *Ber.*, **65B,** 503 (1932); **66B,** 202 (1933); Lauer, K., and Oda, R., *Ber.*, **69B,** 137 (1936); Haack, E., *Ber.*, **62B,** 1771 (1929); Barnett, E., Cook, J. W., and Matthews, M. A., *Ber.*, **60,** 2353 (1927); Clar, E., *Ber.*, **62B,** 350 (1929); **63B,** 112 (1930); Clar, E., and Guzzi, A., *Ber.*, **65B,** 1521 (1932); Fieser, L. F., and Hershberg, E. B., *J. Am. Chem. Soc.*, **57,** 1681 (1935); Obreimov, I., and Prichotjko, A., *Physik. Z. Sowj.*, **1,** 203 (1932).

[23] Fritsche, *J. prakt. Chem.*, **101,** 337 (1866).

[24] Elbs, K., *J. prakt. Chem.*, **44,** 467 (1891).

[25] Orndorff, W. R., and Cameron, F. K., *Am. Chem. J.*, **17,** 658 (1893).

[26] Downs, C. R., U. S. P. 1,303,639, May 13, 1919; *Chem. Abs.*, **13,** 1862 (1919).

[27] Capper, N. S., and Marsh, J. K., *J. Chem. Soc.*, 724 (**1926**).

[28] Luther, R., and Weigert, F., *Sitzb. Akad. Wiss. Berlin,* 828 (**1904**); *J. Chem. Soc.*, **86,** ii 463 (1904); *Z. physik. Chem.*, **51,** 297 (1905); **53,** 385 (1905).

[29] Lauer, K., and Oda, R., *Ber.*, **69B,** 137 (1936).

[30] Weigert, F., *Z. physik. Chem.*, **63,** 458 (1908); Byk, A., *Ibid.*, **62,** 454 (1908).

[31] Weigert, F., *Naturwiss.*, **15,** 124 (1927).

[32] Clar, E., *Ber.*, **65B,** 503 (1932).

[33] Schönberg, A., *Trans. Faraday Soc.*, **32,** 514 (1936).

[34] Volmer, M., and Riggert, K., *Z. physik. Chem.*, **100,** 502 (1922).

[35] Suzuki, M., and Volmer, M., *Naturwiss.*, **23,** 197 (1935).

[36] Orndorff, W. R., and Megraw, H. A., *Am. Chem. J.*, **22,** 152 (1899); Weigert, F., and Krüger, O., *Z. physik. Chem.*, **85,** 579 (1913).

[37] Clar, E., *Ber.*, **65B,** 503 (1932); **68B,** 2066 (1935).

Anthraquinones [38]

Anthraquinone has five bands between 4250 and 3600A, one broad band between 3500 and 2850A and four bands between 2800 and 2300A. Methylanthraquinones and their mono- chlor-, brom- and nitro- derivatives have been observed by Schaarschmidt and Kasai [39] to change from a yellowish-white to a brown color on exposure to a mercury arc. Various ones exhibit the following order of decreasing sensitiveness: 4-chloro-1-methylanthraquinone, 2-methylanthraquinone, 1-methylanthraquinone, 3-chloro-2-methylanthraquinone, 1-chloro-2-methylanthraquinone, 1-chloro-2-bromomethylanthraquinone, 1,3-dimethylanthraquinone. (1,3-Dimethylbenzophenone was not appreciably affected when similarly treated.) The change, at least in the first of these, occurs in a vacuum or in nitrogen as well as when air is present. The change is therefore considered to consist in a transformation into a highly colored quinonoid modification which is not completely reconverted into the original form when rapidly crystallized from alcohol.

Eckert [40] has noted that when 2-methylanthraquinone in acetic acid is exposed for a long time to sunlight with free access of air, the solution becomes increasingly turbid with formation of, chiefly, 2 anthraquinonecarboxylic acid, together with an alkali-insoluble product, which is very probably 2,2′-dianthraquinonylethane. Other derivatives of 2-methylanthraquinone and of 1-methylanthraquinone react in the same way, although less markedly. The oxidation of the former proceeds much more slowly or not at all in other solvents such as toluene, which is itself oxidized to benzoic acid.

He also observed [41] that a solution of potassium anthraquinone-1-sulfonate in hydrochloric acid (1:1) on exposure to light evolves chlorine and yields 1-chloroanthraquinone. Potassium anthraquinone-1,8-disulfonate similarly forms 1,8-dichloroanthraquinone, but the 1,5-disulfonate yields mainly the 1-chloro-5-sulfonate and only little of the 1,5-dichloroanthraquinone. Sodium anthraquinone-2,6-disulfonate affords little 2,6-dichloroanthraquinone and much sodium 2-chloroanthraquinone-6-sulfonate. Anthraquinone-2,7-disulfonic acid yields only products soluble in water. It was possible to isolate 2-chloroanthraquinone-7-sulfonic acid and an isomer. The nitroanthraquinonesulfonic acids react with greater difficulty. 5-, 8-, and 6-Chloro-1-nitroanthraquinones have been obtained from the corresponding sulfonic acids. The bromanthraquinones could not be isolated after exposing solutions of anthraquinone-1 (and -2) sulfonates in hydrobromic acid, although bromine was readily liberated. Eckert and Hampel [42] find that 4,4′-dimethoxy-*meso*-benzbianthrone in chlorobenzene is converted by long exposure to sunlight into naphthobianthrone.

On exposure to light, 3,6′-diacetoxydianthraquinone in benzene solution is slowly changed into diacetoxynaphthadianthrone.[43] A solution of 3,6′-dihydroxydianthraquinone in alcohol on exposure to light deposited crystals which on acetylation gave diacetoxynaphthadianthrone and a little diacetoxyhelianthrone. When an acetone solution of dimethoxydianthrone is evaporated in daylight, the solute becomes rapidly converted into dimethoxynaphthadianthrone and dimethoxyhelianthrone.

[38] For absorption data, see, Hayashi, M., Kawasaki, K., and Nakayama, A., *J. Soc. Chem. Ind. Japan*, **36**, *Suppl. binding*, 123 (1933); Asahina, Y., and Fujikawa, F., *Ber.*, **68B**, 1558 (1935); Jones, D. C. R., and Mason, F. A., *J. Chem. Soc.*, 1813 (**1934**); Hayashi, M., and Nakayama, A., *J. Soc. Chem. Ind. Japan*, **37**, *Suppl. binding* 238, 239 (1934); Marriott, G. J., and Robinson, R., *J. Chem. Soc.*, 1631 (**1934**); Castille, A., *Bull. acad. roy. med. Belg.*, **8**, 74 (1928); Clar, E., *Ber.*, **65B**, 503 (1932).

[39] Schaarschmidt, A., and Kasai, K., *Ber.*, **57B**, 1671 (1924).

[40] Eckert, A., *Ber.*, **58B**, 313 (1925).

[41] Eckert, A., *Ber.*, **60B**, 1691 (1927).

[42] Eckert, A., and Hampel, J., *Ber.*, **60B**, 1693 (1927).

[43] Perkin, A. G., and Yoda, G., *J. Chem. Soc.*, **127**, 1884 (1925).

Weber [44] observed that the resulting dyes were off-color when textiles which had been dipped in solutions of the leuco- compounds of certain halogen-containing anthraquinone and indigoid dyes were exposed to sunlight before oxidation. He regarded this as due to dehalogenation, since the color produced in each case corresponded to that of the halogen-free dye. This suggested a method for the removal of halogen from compounds of the anthraquinone series. Goldstein and Gardner [45] applied it with success in a number of cases. The effect is due to visible rather than to ultraviolet light. 1- and 2-Chloro-, 1- and 2-bromo-, and 1-chloro-4-hydroxyanthraquinone were exposed in alkaline sodium hydrosulfite solutions to a 500-watt Eastman "Floodlight" with exclusion of air. The anthrahydroquinones were then oxidized by air and the amount of dehalogenation calculated from the halogen content of the crude product. The final product from each of the halogen anthraquinones was identified as anthraquinone and that from 1-chloro-4-hydroxylanthraquinone as α-hydroxyanthraquinone. The α-halogen is much more readily removed than β-halogen, and bromine more readily than chlorine.

Anthrahydroquinol-α-carboxylic lactones in alkaline, acid or neutral solutions are sensitive to air, especially in benzene or xylene in light.[46] The 2-methyl derivative of anthrahydroquinol-1-carboxylic lactone gave chiefly with typical oxidizing agents 2,2′-dimethyl-9,9′-dihydroxyl-1,1′-dicarboxylic dilactone. Aqueous and especially alcoholic alkalies dissociate the latter with formation of an olive-green solution containing the salts of the anthraquinone and the anthrahydroquinol acids apparently in quinhydrone-like combination. Probably the primary step is a dissociation into an anthoxyl radical with univalent oxygen. Exposure in acetic acid to ultraviolet light, and heating in certain organic solvents, apparently also brings about a similar dissociation.

Much has been written in regard to the use of anthraquinone derivatives in facilitating photochemical oxidations of a wide variety of organic compounds. The anthraquinone in light acts as an oxygen carrier, the carbonyl groups being reduced to carbinols. These regenerate the anthraquinone on shaking with air. When dextrose is the oxygen acceptor, this reaction occurs also in the dark.[47] Other quinones (benzoquinone, naththoquinone, acridone) xanthone and benzophenone are less effective. Anthraquinone is unable to oxidize naphthalene in acetic acid to phthalic acid.

Kreidl [48] uses as catalysts, in effecting such oxidation reactions, ring-system hydrocarbons containing at least three condensed nuclei, such as anthracene; substitution products of such hydrocarbons; substances of quinonoid type, with a ring system containing at least three condensed nuclei and of a lower state of oxidation with respect to at least one of the quinonoid carbon atoms than corresponds to anthraquinone; substitution products of such substances; or hydrogenated products of hydrocarbons with a ring system containing at least three condensed nuclei or their substitution products. Nozicka [49] effected such photochemical oxidation processes in the presence of a catalyst of the anthraquinone type in conjunction

[44] Weber, A. E., *Dyestuffs*, **33**, 1 (1933); *Am. Dyestuff Reptr.*, **22**, 157 (1933); *Chem. Abs.*, **27**, 3336 (1933); *Brit. Chem. Abs.*, **1933B**, 344.

[45] Goldstein, A. E., and Gardner, J. H., *J. Am. Chem. Soc.*, **56**, 2130 (1934).

[46] Scholl, R., and Renner, F., *Ber.*, **62B**, 1278 (1929).

[47] Pfeilsticker, K., *Biochem. Z.*, **199**, 8 (1928).

[48] Kreidl, I., U. S. P. 1,971,042, Aug. 21, 1934; *Chem. Abs.*, **28**, 6066 (1934).

[49] Nozicka, F., German P. 526,195, October 27, 1929; *Chem. Abs.*, **25**, 4184 (1931).

with one or more auxiliary catalysts, such as sodium or potassium hydroxide, active carbon, inorganic gels or oxides of copper, bismuth, iron, vanadium or silver. Illustrative reactions[50] are the oxidation of toluene to benzoic acid, of paraffin oil to fatty acids, of lepidine to cinchoninic acid, etc.[51]

Oxidation of Anthracene. Hibberd[52] states that anthracene exposed to daylight or to light of the Fade-Ometer (See Chapter 30) becomes yellow or brown and gives a positive reaction for anthraquinone. Dufraisse and Gérard[53] state that under certain conditions anthracene combines with oxygen to form a colorless, crystalline photo-oxide of the structure $C_6H_4 \cdot CH \cdot C_6H_4 \cdot CH$ (with an O·O bridge). This is stable at ordinary temperatures, but at 120°C. decomposes explosively without evolution of oxygen. It can be titrated with potassium iodide, which reduces it to anthranol or oxanthrol, but isomerization and subsequent oxidation to other products also occur. The photo-oxide resembles oxanthrone in state of oxidation and in giving, with hydrochloric acid and hydrobromic acid, 10-chloro- and bromoanthrone, respectively. 9-Phenyl-10-iodoanthracene is irregularly photo-oxidizable. 9-Phenyl-10-carboxyanthracene and its methyl ester are also photo-oxidizable, but the carboxyl group apparently hinders the addition of oxygen. The photo-oxide of 9-phenylanthracene can be obtained in only 30 per cent yield.[54]

Although the 9,10-diarylanthracenes form photo-oxides that dissociate on heating, that of anthracene explodes at 120°C., and that of 9-phenylanthracene decomposes at 155° with emission of about 12 per cent of oxygen.[55] 10-Methyl- and 10-ethyl-9-phenylanthracene photoöxides behave more like 9-phenylanthracene than like the diaryl compounds, decomposing at 170° and 200° with evolution of 20 and 34 per cent of oxygen, respectively.

To determine whether the reason that anthracene photo-oxide does not liberate all its oxygen on pyrolysis while the corresponding diphenylanthracene photo-oxide liberates 95 per cent of its oxygen[56] might be the greater oxidizability of hydrogen as compared with the phenyl group, Dufraisse and Priou[57] studied the *meso*-dimethoxy-photo-oxide in the expectation that the methoxyl radical would be less oxidizable than the phenyl. They found, however, that this explanation does not hold, since the compound is unstable in light, especially when in solution. It melts at 145°C., with decomposition, leaving a residue of anthraquinone. Willemart[58] found 9,10-di-α-naphthylanthracene, as well as the di-β-naphthyl compound, when exposed to sunlight in the presence of air to yield photoöxides. The latter heated at 180-200°C. lose oxygen and regenerate the hydrocarbons.[59]

[50] French P. 702,183, Aug. 27, 1930, to Vereinigte Chemische Fabriken Kreidl Heller & Co.; *Chem. Abs.*, **25,** 3919 (1931); Austrian P. 151,652, Nov. 25, 1937; *Chem. Abs.*, **32,** 2029 (1938).

[51] See also German P. 624,964, Feb. 1, 1936, to Kreidl, Heller & Co.; French P. 739,711, July 6, 1932; German P. 536,195, Oct. 27, 1929.

[52] Hibbert, E., *J. Soc. Dyers Colourists,* **44,** 377 (1928); *Brit. Chem. Abs.*, **1929B,** 88.

[53] Dufraisse, C., and Gérard, M., *Compt. rend.*, **201,** 428 (1935); **202,** 1859 (1936). For a more detailed study of the influence of solvents on photopolymerization and photoöxidation, which have as common intermediate an unstable dimer, see Dufraisse, C., and Gérard, M., *Bull. soc. chim.*, **4,** 2052 (1937).

[54] Dufraisse, C., Velluz, L., and Velluz, Mme., *Compt. rend.*, **203,** 327 (1936). Since phenanthrene and naphthalene structures do not form photo-oxides, this is a phenomenon different from the accelerated photo-oxidation of numerous unsaturated compounds. Dufraisse, C., and Priou, R., *Bull. soc. chim.*, **5,** 611 (1938).

[55] Willemart, A., *Compt. rend.*, **203,** 1372 (1936); *Bull. soc. chim.*, **4,** 357 (1937).

[56] Dufraisse, C., and LeBras, J., *Bull. soc. chim.*, **4,** 349 (1937); Dufraisse, C., Velluz, L., and Velluz, Mme., *Ibid.*, **4,** 1260 (1937); Velluz, L., and Velluz, Mme., *Bull. soc. chim.*, **5,** 192, 606, 1073 (1938); *Chem. Abs.*, **32,** 3379 (1938).

[57] Dufraisse, C., and Priou, R., *Compt. rend.*, **204,** 127 (1937).

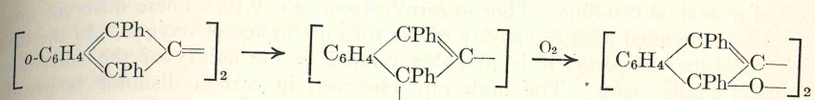
[58] Willemart, A., *Compt. rend.*, **201,** 1201 (1935).

[59] See also Willemart, A., *Compt. rend.*, **202,** 140 (1936); *Bull. soc. chim.*, **4,** 510 (1937) for the tolyl derivatives.

9-Methyl (or ethyl)-anthracene polymerizes when irradiated. At the melting points of the polymers, the original hydrocarbons are regenerated, but under certain conditions photo-oxides may be obtained which do not evolve oxygen on heating. Dimethyl (9,10)-derivatives of 9-phenylanthracene do not polymerize.[60]

Acridine and 9-phenylacridine give no light-stable photo-oxides.[61]

Naphthacenes. The red hydrocarbon rubrene, $C_{42}H_{28}$, (tetraphenyl rubene) forms a peroxide when its benzene solution containing dissolved oxygen is exposed to visible or ultraviolet light; no oxidation occurs in darkness.[62] The peroxide is stable in solution, colorless and has a molecular weight of 561. Schönberg[63] believes light converts rubrene into an activated diradical form, which adds oxygen to form the peroxide.



Rubrene *Diradical* *Peroxide*

The presence of hydroquinol and pyrocatechol and their methyl ethers retards the reaction. Dissociation of the peroxide into rubrene is accompanied by the emission of light. If a benzene solution of the brown form (which owes its color to the presence of an impurity and is really yellow) is exposed to sunlight and then heated to 80°C., the solution becomes luminous. Irradiation destroys the impurity, but the solution can again be activated by sunlight. When in the solid state, the yellow form is luminous after exposure to sunlight, but it is not luminous in solution.

The quantum efficiency of the formation of the peroxide of rubrene rises to unity at concentrations greater than 0.01 molar, and is independent of wave-length between 3660 and 5460A.[64] Bowen and Steadman believe the reaction to depend on termolecular collisions between an activated and a normal rubrene molecule and an oxygen molecule.

The mechanism of the reaction has been the subject of recent discussion.[65] Schumacher believes an excited rubrene molecule R^- incapable of forming a stable RO_2 molecule by collision with an oxygen molecule, unless it has previously collided with another R molecule to give a long-lived R* molecule which can form a stable oxide. Another possibility, applicable to the results at low oxygen pressures, is for an R^- molecule to form with oxygen an unstable RO_2 molecule which can be stabilized by collision with another R molecule. Neither excited

[60] Willemart, A., *Compt. rend.*, **205,** 866, 993 (1937); *Bull. soc. chim.*, **5,** 556 (1938); *Chem. Abs.*, **32,** 4976 (1938). For 9-alkyl-10-phenyl-anthracenes, see *Bull soc. chim.*, **4,** 1447 (1937).

[61] Dufraisse, C., and Houpillart, J., *Bull. soc. chim.*, **5,** 626 (1938).

[62] Moureu, C., Dufraisse, C., and Lotte, P., *Compt. rend.*, **190,** 148 (1930); Moureu, C., Dufraisse, C., and Butler, C., *Ibid.*, **183,** 101 (1926).

[63] Schönberg, A., *Ber.*, **67B,** 633 (1934).

[64] Bowen, E. J., and Steadman, F., *J. Chem. Soc.*, 1098 (1934).

[65] Gaffron, H., *Biochem. Z.*, **264,** 251 (1933); Schumacher, H. J., *Z. Elektrochem.*, **42,** 522 (1936); Koblitz, W., and Schumacher, H. J., *Z. physik. Chem.*, **B35,** 11 (1937); *Brit. Chem. Abs.*, **A,** I, 255 (1937); Gaffron, H., *Z. physik. Chem.*, **B37,** 437 (1937); *Brit. Chem. Abs.*, **A,** I, 40 (1938); Schumacher, H. J., *Z. physik. Chem.*, **B37,** 462 (1937).

oxygen molecules nor long-lived excited R molecules are believed to play an important part in the reaction. Gaffron found that at small concentrations the oxygen pressure affects the quantum yield. From data on the quantum yield at small oxygen pressures, he concluded that there must be, in addition to the ordinary, short-lived, active form of rubrene, another comparatively long-lived (10^{-2} to 10^{-1} second) active form during the life of which every collision leads to reaction. Schumacher has finally suggested that Gaffron may not have measured the pure rubrene oxidation. The discussion of the mechanisms, too intricate to be given here, is of some significance for the theory of photosensitized processes, since Gaffron views the oxidation, at least in the case of high rubrene concentrations, as what may be called a self-sensitized process.

The relative rates of oxidation of tetraphenylrubrene in 1 : 10,000 dilution in ten organic solvents in the light of a carbon arc have been determined by Dufraisse and Badoche,[66] that in benzene being taken as unity. The highest value, 9, was obtained in carbon disulfide. That in nitrobenzene was 0.10. These different rates seem to be connected with the ability of the solvents to accept oxygen. In the case of nitrobenzene, however, it is probably related to the ability of the solvent to extinguish fluorescence. The high rate observed in carbon disulfide is greatly reduced by the addition of ether. Acetone had little effect on the rate in nitrobenzene. In general, the oxidation is the more rapid the more nearly the absorption maximum in the given solvent approaches the red, but definite relations could not be deduced.

It has been suggested that pure oxygen can be extracted from air by way of the dissociable photo-oxide of rubrene or of *meso*-diphenylanthracene.[67]

The compound formed by exposure of a chlorophyll solution to light in the presence of an acceptor [68] has a diradical character similar to that obtained in the case of rubrene.[69]

A review of the literature on the synthesis and photochemical properties of the naphthacenes (a term used to replace rubrenes) has been given by Dufraisse and Horclois.[70] Naphthacene forms a photo-oxide, $C_{18}H_{12}O_2$, colorless needles, which gives no oxygen on decomposition. Diphenyl-9-10-naphthacene gives a photo-oxide, $C_{30}H_{20}O_2$, which liberates iodine from potassium iodide, but melts at 160° without giving oxygen. 1,2,3,4-Tetrahydro-9,10-diphenylnaphthacene gives a photo-oxide, $C_{30}H_{24}O_2$, which regenerates the original hydrocarbon and liberates 80 per cent of its oxygen at 200°C. The presence of two hydrogen atoms in the 1,1′-positions in rubrenes suppresses the reversibility of absorption of oxygen.[71]

1,1′-*Bis*(*p*-tolyl)-3,3′-diphenyl-5,5′-dimethylrubrene, $C_{46}H_{36}$, forms red solutions which are decolorized by light in the presence of air with the formation of a peroxide.[72] Dufraisse and Loury [73] found ethyl-1,1′-diphenylrubrene-3,3′-dicarboxylate to form a photo-oxide which at 190°C. loses a little oxygen and much carbon dioxide. Solutions of 1,1,3′-triphenylrubrene-3-carboxylate in alcohol are moderately rapidly decolorized by sunlight, but the corresponding acid is much more

[66] Dufraisse, C., and Badoche, M., *Compt. rend.*, **200,** 1103 (1935).
[67] Dufraisse, C., and Le Bras, J., *Bull. soc. chim.*, **4,** 349 (1937).
[68] Gaffron, H., *Biochem. Z.*, **264,** 251 (1933); *Chem. Abs.*, **27,** 5763 (1933).
[69] Schönberg, A., *Annalen*, **518,** 299 (1935); Müller, E., and Müller-Rodloff, I., *Annalen*, **517,** 134 (1935); *Chem. Abs.*, **29,** 5320 (1935).
[70] Dufraisse, C., and Horclois, R., *Bull. soc. chim.*, **3,** 1872, 1880 (1936); *Brit. Chem. Abs.*, **A,** 1499 (1936).
[71] Dufraisse, C., and Loury, M., *Compt. rend.*, **200,** 1673 (1935); *Chem. Abs.*, **29,** 5108 (1935).
[72] Dufraisse, C., and Monier, J. A., Jr., *Compt. rend.*, **196,** 1327 (1933); see also Dufraisse, C., and Chovin, P., *Compt. rend.*, **197,** 1127 (1933).
[73] Dufraisse, C., and Loury, M., *Compt. rend.*, **199,** 957 (1934).

stable.[74] The residues from the resulting solution are complex and, when heated, evolve mainly carbon dioxide mixed with from 3.7 to 6.0 per cent of the amount of oxygen to be expected from a peroxide. In sunlight, a solution of 0.0678 gm. of 9,10,11-triphenylnaphthacene (triphenylrubrene) in 2.5 cc. of benzene absorbed one mole of oxygen in an hour and became colorless. Larger-scale work led to the isolation of the photo-oxide, $C_{36}H_{24}O_2.C_6H_6$ which, on heating under various conditions, liberated from 6 to 15 per cent of oxygen. It is probably an internal 11,12-dioxytriphenylnaphthacene.[75]

Hexabromotetraphenylrubrene in benzene in direct sunlight forms colorless crystals of the peroxide, which decomposes to yield 76 per cent of the theoretical amount of oxygen at 150°C. in thirty to forty-five minutes or in fifteen minutes at 200°C.[76]

Other Hydrocarbons

Chrysogen, the yellow impurity occurring with anthracene, and probably a hydrocarbon, is easily destroyed by exposure of its xylene solution to light. It apparently undergoes polymerization to a colorless substance in a manner similar to anthracene.[77]

In the production of skin cancers in mice by the repeated application of a 1-per cent solution of 1,2-benzopyrene in benzene, sunlight exerts an accelerating influence.[78]

A benzene solution of benzaldehyde and acenaphthene, exposed to sunlight for two years, yielded [79] two polymers of benzaldehyde, one previously observed by Ciamician and Silber,[80] and the other a trimer previously obtained by Mascarelli,[81] a compound corresponding to the addition of a molecule each of acenaphthene and benzaldehyde less a molecule of hydrogen. In addition, there were formed stilbene, isostilbene and resinous material.

The autoxidation of decalin is accelerated by ultraviolet, according to Castiglioni.[82] The exposure of an alcoholic solution of 5-tetraleneacetic acid to the radiation of a quartz mercury lamp yields dihydronaphthylacetic acid.[83]

According to Goldschmidt and Reichel,[84] the yellow product obtained together with fluorenone and $\Delta^{9,9'}$-di-fluorenylene by the atmospheric oxidation of 9-aminofluorene in sunlight, or ultraviolet light, can also be formed with loss of ammonia when oxygen is passed over the base at 75 to 80°C. in darkness. It must be tetrafluorenylhydrazine, its colored solutions containing the radical $(C_{13}H_9)_2N^-$. Optically active, colorless, 3-methoxy-9-phenylfluorene-9-thioglycollic acid turns first yellow and then orange in ultraviolet light. This change occurs also in the

[74] Badoche, M., *Compt. rend.*, **198,** 662, 1515 (1934); **200,** 750 (1935).
[75] Badoche, M., *Bull. soc. chim.*, **3,** 2040 (1936).
[76] Dufraisse, C., and Velluz, L., *Bull. soc. chim.*, **3,** 254 (1936).
[77] Capper, N. S., and Marsh, J. K., *J. Am. Chem. Soc.*, **47,** 2848 (1925). For absorption data on phenanthrene see Goldschmidt, S., and Graef, F., *Ber.*, **61B,** 1858 (1928); Titeica, R., *Bul. soc. romane fiz.*, **35,** 149 (1933); *Chem. Abs.*, **28,** 1618 (1934); Clar, F., and Lombardi, L., *Ber.*, **65B,** 1411 (1932); Askew, F. A., *J. Chem. Soc.*, 509 **(1935).** It is not autoxidizable in light. Benrath, A., and v. Meyer, A., *Chem. Abs.*, **7,** 352 (1913).
[78] Maisin, J., and de Jonghe, A., *Compt. rend. soc. biol.*, **117,** 111 (1934).
[79] De Fazi, R., *Atti accad. Lincei*, **9,** 1004 (1929); *Chem. Abs.*, **24,** 362 (1930).
[80] Ciamician, G., and Silber, P., *Chem. Abs.*, **4,** 1619 (1910).
[81] Mascarelli, L., *R. Accad. Lincei*, **15,** II, 375 (1906).
[82] Castiglioni, A., *Gazz. chim. ital.*, **64,** 465 (1934); *Brit. Chem. Abs.*, **A,** 1184 (1934); Moureu, C., Dufraisse, C., and Chaux, R., *Chem. Abs.*, **21,** 1914 (1927). For the irradiation of squalene, see *J. Soc. Chem. Ind.*, 181 **(1926).**
[83] Schroeter, G., *Ber.*, **58,** 713 (1925).
[84] Goldschmidt, S., and Reichel, L., *Annalen*, **456,** 152 (1927).

case of solutions of phenylfluorenylcarbinols, but the 9-phenylfluorenes are insensitive to light. Racemization is the principal effect of light.[85]

Crude synthetic perylene may be purified by exposing it to a quartz mercury arc.[86] Ether solutions of crude coal-tar show increased ultraviolet transmission after having been similarly irradiated.[87]

On illumination of a cyclohexane solution of carotene, the pressure of oxygen above it in a closed vessel drops initially and reaches a constant value in about three hours. If all or part of the oxygen is then pumped out in the dark, on re-illumination, a pressure rise is observed, indicating an equilibrium between carotene, its oxide and oxygen. But in the case of an octane solution, the oxygen pressure decreases linearly with time without reaching a minimum value.[88]

[85] Lifschitz, I., *Rec. trav. chim.*, **54,** 397 (1935); *Chem. Abs.*, **29,** 5437 (1935).

[86] Postovskii, I. Y., and Bednyagina, N. P., *J. Gen. Chem. (U. S.S. R.)*, **7,** 2929 (1937); *Chem. Abs.*, **32,** 5396 (1938).

[87] Herrick, J. F., and Sheard, C., *Proc. Soc. Exptl. Biol. Med.*, **26,** 33 (1928).

[88] Baur, E., *Helv. Chim. Acta*, **20,** 402 (1937).

Chapter 27

Compounds with Heterocyclic Rings

Oxygen-containing Rings

Essential Oils. The spontaneous transformation of solutions of various odorous substances into a colloidal state by exposure to light has been investigated by Zwaardemaker and Hogewind.[1] In the case of several substances the change occurred only in the presence of ultraviolet light and the resulting colloidal particles were negatively charged. Among the substances studied were eugenol, cresol, guaiacol, carvacrol, citral, cumidine, thymol and hypnone.

A sample of dark yellow distilled lavender oil was found by Quilico[2] to be progressively decolorized by exposure to ultraviolet rays without losing its original fragrance. After one hour, 20 cc. were colorimetrically equivalent to only 19.5 cc. This became 11.5 cc. after 7, 2.5 after 14 and 0.5 cc. color equivalent after 21 hours. Eucalyptus oil was decolorized slightly more rapidly. It was suggested that the formation of oxygenized products caused the slightly lower results in the lavender oil. The essential oil of *Monarda fistulosa* behaves in the opposite manner, becoming brown when exposed to light, according to Badzynski.[3]

Absorption data on a series of oils have been given by Morton[4] and may serve as an aid in the identification of constituents. Maxima are found at 3070 and 2370A (wintergreen), 2810 and 2435A (almond), 2810A (clove), 2770A (thyme), 2860A (cinnamon and cassia), 2850 and 2330A (sassafras), 3110A (lemon), 2380A (mustard), 2320A (cade). Wormseed and mace oils show but little selective absorption. Previous observations on the use of ultraviolet spectrograms in the identification of essential oils were due to Boyer.[5]

It is well known that good quality peppermint oil when used in flavoring certain candies or sugar preparations, such as ordinary mint tablets, loses its fine flavor on long standing. In the laboratory of the senior author, a number of samples of such tablets were exposed to the action of ultraviolet in order to test the stability of certain mint oils in the manufacture of confections. It was found that a few hours' exposure afforded approximately the same aging effect as standing on the shelves for a period of several months. The procedure appears to be a ready method of testing materials of this class to determine quickly their keeping qualities.

It is said that the oxidation of Russian turpentine is more rapid in sunlight

[1] Zwaardemaker, H., and Hogewind, F., *Proc. Akad. K. Wetensch. Amsterdam*, **21,** 131 (1918); *J. Chem. Soc.*, **116,** ii, 14 (1919).

[2] Quilico, A., *Rivista ital. essenze profumi*, **10,** 148 (1928); *Chem. Abs.*, **23,** 2784 (1929).

[3] Badzynski, S., *Wiadomoscki Farm.*, **60,** 689 (1933); *Chem. Abs.*, **28,** 1815 (1934).

[4] Morton, R. A., *Perfumer and Essential Oil Record*, **20,** 258 (1929). See also Harvey, E. H., *J. Am. Pharm. Assoc.*, **19,** 1173 (1930); *Chem. Abs.*, **25,** 5850 (1931); van Os, D., and Dykstra, K., *J. pharm. chim.*, **25,** 437, 485 (1937).

[5] Boyer, J., *Am. Perfumer*, **17,** 389 (1922).

[6] Korotkov, K. N., *Mem. Belloruss. State Acad. Agr.*, **5,** 16 (1927); *Brit. Chem. Abs.*, **B,** 650 (1929); *Lesokhim. Prom.*, **4,** No. 11, 6 (1935); *Chem. Abs.*, **30,** 8658 (1936).

[7] Jorissen, W. P., and Vollgraff, J. A., *Chem. Weekblad*, **12,** 93 (1915); *J. Chem. Soc.*, **108**(ii), 80 (1915).